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## Electromagnetic Fields in Water Treatment

Robert H. Fagan  
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ELECTROMAGNETIC FIELDS IN  
WATER TREATMENT

BY

ROBERT H. FAGAN  
M.S., Georgia Institute of Technology, 1940

RESEARCH REPORT

Submitted in partial fulfillment of the requirements  
for the degree of Master of Science in Environmental  
Systems Management in the Graduate Studies Program of  
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Orlando, Florida  
August 1974



## ELECTROMAGNETIC FIELDS IN WATER TREATMENT

by

Robert H. Fagan

## ABSTRACT

Properties and characteristics of colloidal systems are reviewed with a discussion of colloid systems to be found in natural and waste-waters. Current electric and magnetic field theory are reviewed and summarized to provide practical application of the theory to engineering problems in the environmental field.

Literature of colloidal reactions to electrical and magnetic fields is discussed and reviewed to ascertain areas of potential application of electric and magnetic phenomena to natural and wastewater treatment systems having objectionable colloid suspensions.

It is concluded that application of electrical fields (electrophoresis) does not currently hold much promise for practical applications in water treatment systems. However, an understanding of colloid systems and electrophoresis is strongly recommended for personnel involved in chemical treatment of waters. It is shown that there has been considerable research and many applications of magnetic field treatment of waters by the Russians, most analysis of which is performed in an empirical manner, that tends to cloud the phenomena with an aura of mysticism. Practical applications of magnetic field phenomena to water treatment systems involving ferromagnetic colloidal suspensions appears promising and research into this area is recommended.

*Waldron M. McLellon*  
Waldron M. McLellon, PhD, P.E.  
Committee Chairman



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## CHAPTER I

### INTRODUCTION

In spite of our many advances in the physical sciences, space mechanics, nuclear physics and chemistry since the time of Sir Isaac Newton (circa 1700), our knowledge today of the cause and reason of gravity, electric fields, and magnetic fields remains pitifully small. We have studied, measured and analyzed the effects of these phenomenon and can predict with good accuracy and reliability the effects that accrue in the use of these force fields on physical matter. In the last twenty to thirty years interest has increased in microscopic and submicroscopic particles suspended in gases, liquids and solids; and in their composition and behavior under various externally applied conditions. In this paper we are extracting a very small portion of this broad field of investigation to look at what we know and what we suspect or hypothesize on the behavior of colloids suspended in a liquid medium (usually water) and acted upon by an applied electrical or magnetic field.

Literature on the commercial use and applications of magnetic fields is very limited and "there appears to be a wide technology transfer gap between the state of advanced magnet technology used in basic research and the state of commercial magnetic separation practice.<sup>1</sup>" Commercial applications in the U.S. have been directed almost exclusively



to mining and steel making processes involving the removal or recovery of iron oxides from liquid suspensions.

The application of electrical fields to colloid suspensions, on the other hand, has been quite extensive, primarily in the medical field. Considerable literature exists in this area dealing with theoretical, research, and application of electrical fields on colloidal suspensions. However, its application to water treatment processes appears very limited and is reviewed herein. Removal and/or recovery of colloidal suspensions from water is normally achieved by an "electrical/ionic" process involving use of inorganic precipitates or synthetic long-chained high-molecular-weight (100,000 or greater) organic polyelectrolytes (e.g. polyacryamides,  $\text{R-CH}_2-\underset{\text{CONH}_2}{\underset{|}{\text{CH}}}-\text{R}'$ ; acids,  $\text{R-COO}^- \text{H}^+$ ; and salts,  $\text{R-COO}^- \text{Na}^+$ ). These polyelectrolytes can perform a double function of neutralization of the zeta potentials causing colloids to repel each other, and providing a chain linkage or bridge between particles bonding themselves to the chain molecule. However, it is the intent in this paper to investigate the potential application of electric and magnetic fields to the more general problems of water and wastewater treatment processes, to ascertain any known limitations to such applications, and to identify areas requiring more research and study in the immediate future.

Potable water treatment is currently accomplished using aeration, chemical, and filtering processes to remove colloidal and other contaminants, among others. Wastewater treatment normally requires additional processes for removal of solids because of higher concentrations of



contaminant and pathogenic materials, and the presence of putrescible organics. With increasing amounts of pollution causing material being generated and higher standards of water quality being established, more extensive wastewater treatment facilities and processes are required to meet our needs. Thus the activated sludge process utilizing biological digestion and tertiary treatment (designed to remove contaminants remaining after primary and secondary treatment) have become a part of the additional tools (processes) available to meet man's needs. Chemical processes such as adsorption, coagulation, precipitation and ion-exchange are closely related and controlled by electrical and magnetic characteristics of colloids. However they will be excluded from this paper except insofar as they may enhance or hinder the separation of colloids from their substrate by electrical or magnetic processes.

The writer was fortunate to have access to copies of publications and articles collected over a period of years by Dr. W. M. McLellon, Gordon J. Barnett Professor of Environmental Systems Management, Florida Technological University, Orlando, Florida. Collation of these papers resulted in a division of the papers into three categories: chemical coagulation and flocculation papers, electrophoresis or electrokinetic papers, and finally those that dealt with magnetic properties and magnetic field reaction of colloids. The quantity of papers, the extent of current knowledge, and the applicability of these different process methods appear to be in the same order of magnitudes in that there appear to be very little effort directed to magnetic effects on colloids, considerably more on electrophoresis, and volumes on chemical



treatments. Similar disparity in literature availability existed in the literature search conducted.



## CHAPTER II

### PROPERTIES OF COLLOID SYSTEMS

#### A. Physical

Krulyt<sup>2</sup> provides an excellent and detailed analysis of the properties of colloidal particles. He points out the arbitrary nature of selecting boundary limits for kinetic units having properties that change with size. In general, when we speak of colloidal suspensions today, we are normally interested in that area of matter having sizes greater than a single molecule but less than settleable solids, emulsions, and solid suspensions. Krulyt chose a lower dimension of 1  $\mu$  (approximately  $10A^0$ ) and an upper limit of about  $1\mu$  ( $10,000A^0$ )\*; but recognized that shape has an effect and quotes a proposal of H. Staudinger, where colloids are defined as particles with  $10^3$  to  $10^9$  atoms. This of course doesn't answer the problem since it is possible today to synthesize molecules of molecular weights of 30,000,000 or more. Colloid particle sizes are normally considered to range from about  $10A^0$  - some scientists go as low as  $5A^0$  for the smallest dimension - (water molecule diameter is approximately 3 to  $6A^0$  depending on the electron quantum states), which can therefore extend into the soluble range of some compounds, to 1 micron,  $\mu$ , or  $10,000A^0$  (larger particles are normally considered "suspended particles" or supracolloidal. Shapes considered are generally either linear (needle or rod), disc, or spherical. Densities vary depending

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\* the symbol " $\mu$ " is used throughout this paper to represent a micron or one millionth of a meter.



on composition and molecular structure but tend to average out at about 2 for compounds normally found in natural and waste waters.<sup>2</sup> Likewise electrical and magnetic properties vary with composition, however, for purposes of this study we are only interested in those colloids exhibiting a reaction to electrical or magnetic fields as a result of the electrical charge on the particle.

Laboratory use of millipore filters have resulted in a general practice of assuming that if a particle is not filtered out of solution by a  $0.45\mu$  pore membrane it can be considered as "soluble matter."<sup>3</sup> Color as well as a considerable amount of other colloidal-sized organic material will remain with the filtrate of a  $0.45$  millipore filter and would be considered a part of the "soluble fraction" in such cases. Sawyer and McCarty<sup>4</sup> classify colloidal particles as having dimensions in the range of  $1\text{ m}\mu$  to  $100\text{ m}\mu$  which appear too restrictive on the upper end of the scale. For this paper, and the generally accepted colloid size definition, particles having at least one dimension greater than  $1\text{ m}\mu$  and with no dimension exceeding  $1\mu$  will be considered "colloidal" and those in the range of  $1 - 100\mu$  as "supracolloidal."

The one physical characteristic that tends to separate colloids from macro-particles and suspended solids is the great surface area of the colloidal particles for the weight or mass of material involved. It has been shown that a cube of  $1\text{ cm}$  on a side and having an exposed surface area of six square cm when divided into colloidal sized cubes of  $10\text{ m}\mu$  dimensions will provide a surface area of 600 square meters, or about  $1/7$  acre. It is this large surface area that results in colloidal



phenomena dealing mainly with adsorption reactions with ions and other colloids.

For practical purposes, we are normally concerned in water treatment with those particles that do not settle from suspension in a period of three to six hours in the clarifier. Thus shape (drag coefficient) and density of particles become factors of interest in colloidal suspensions. Particle shapes are normally classified into spherical, disc, and rod (needle). While the sphere is normally considered to have the lowest drag coefficient, particles with an ellipsoidal or tear drop shape can have lower coefficients than a sphere providing the laminar boundary layer separation is less than that of a sphere and the increased wetted area skin friction drag does not exceed the reduction due to boundary layer separation. It should also be noted that particles having magnetic properties normally have a linear dimension and tend to form lattice structures when activated by induced magnetism.

Material density is a function of the atomic molecular weights of the material, their number and molecular arrangement or structure. Gravity forces on colloidal particles are proportional to the difference of the density of the particle and the solution it is suspended in. Using Stokes' equation<sup>5</sup> the sedimentation velocity can be determined based on spherical particle radius,  $a$ , and the viscosity coefficient,  $\eta$ , by the following formula:

$$v = \frac{4/3 \pi a^3 \cdot g}{6 \pi \eta a} (d_1 - d_2)$$

where  $d_1$  = density of particle and  $d_2$  = density of medium. While metal particles may achieve densities as high as 20, particle densities of



about 2 represent a normal average<sup>2</sup>. Krutz considered that a sedimentation velocity of the order of 1 mm per day would be considered negligible since accidental thermal convection would be expected to counteract such settling. This results in an equivalent spherical particle with a density of 2 having a diameter of approximately  $0.15\mu$ .

For a spherical particle having a sedimentation velocity of 0.008 cm/sec (approximately 1 ft./hr. in a clarifier) and a density of 2, the particle diameter is approximately  $6\mu$ , which can probably represent the upper limit of "colloidal" size in water treatment processes.

For colloidal particles that remain in suspension in water but have a density considerably greater than water, there must exist other forces, greater than the gravitational forces, that act upon the particles to maintain their suspension. Further one can assume that forces that cause this suspension are related to the size of the particle suspended since when dispersing forces on colloids are chemically or electrically neutralized the particles coagulate; flocculate, and sink to the bottom (if they have a greater density than the surrounding medium).

Brownian motion, a continuous agitation of colloidal particles caused by unbalanced impacts with molecules of the surrounding medium (the motion can be observed with a microscope when a strong beam of light is caused to traverse the solution across the line of sight), tends to distribute these colloidal particles as uniformly as possible throughout the solution. This, when combined with gravitational force, can result in a layered system in equilibrium having a particle distribution similar to our air atmosphere, in the liquid solution.



## B. Electrical

One of the three attractive forces that can be exerted between colloid particles is the van der Waals force - the other two are coulomb electrical and chemical. Van der Waals force is electrical in nature but is distinguished from coulombic forces involved in charge attraction and repulsion in that the particles must be electrically neutral initially; the force decreases very rapidly with distance and is always attractive. Current theory holds that van der Waals forces are the result of permanent or induced dipole interaction between particles and molecules wherein an ion-dipole or dipole-dipole attraction is achieved by orientation of the opposite charged polar ends of the two particles close to each other. The force resulting from an ion-dipole interaction decreases approximately with the cube of the distance separating the particles, and for nonpolar particles where the dipole is induced, the attractive force decreases with the seventh power of the distance.<sup>6</sup>

Gravitational forces between particles are normally not considered because even when the particles are touching, the attractive force is negligible compared to the other forces acting on the particles and to the field of the earth. Likewise, chemical forces involving the exchange of electrons between atoms, or covalent bonding, are not an element of colloid systems although they are very strong when exerted at extremely short ranges.

Colloidal particles in water normally exhibit electrical properties by exhibiting a static electrical charge. This charge results in an anti-coagulating and dispersive reaction of particles through



the repulsion force of like charges. Further, this has created a field of study on the phenomenon of "electrophoresis" which is the movement of charged particles suspended in a liquid under the influence of an applied electrical field. Electrophoresis has considerable application in the medical and organic chemistry fields since cellular reactions occur as a result of electrophoresis. Briefly, current theory is that colloidal particles acquire their charge because of ionization of their surface molecules and adsorption of ions.<sup>7</sup> Because most of the ionizing groups are weak electrolytes and because binding energies for adsorption are of the order of magnitude of thermal energies, the surface charge situation must be described as an equilibrium between ions bound to the surface and hydrolyzed ions in solution. The boundary between two phases (the particle and the medium) is looked upon as a layer of finite dimensions and not as a plane, the layer having a thickness of several hundred Angstrom ( $\text{\AA}$ ) units for large colloid particles. Thus there is obtained an ionic layer localized in a plane adjacent to, say, the solid phase of the particle with a second ionic layer of opposite charge located in an adjacent layer but in the liquid phase of the medium. This second layer has the character of a space charge and extends fairly far into both phases. In this second (or outer) layer the counter ions would remain very close to the interface due to the coulomb force acting upon them. However the irregular Brownian motion tends to diffuse these ions away from the interfacial surface of the two layers. The two layers thus establish an equilibrium, with the ions in the outer layer having a first order distribution such that the zeta potential,  $\zeta$ , drops as distance from the interface increases - high electrolytic concentrations



and high valency results in a more rapid reduction of the zeta potential with distance than for low concentrations and valency. Thus when the colloidal particle is placed in an electric field the electrophoretic velocity of the particle is (as a first order approximation) proportional to the  $\zeta$ -potential rather than the particle charge, i.e. the adhering layer to the particle with its counterions has reduced the particle charge strength. Thus in a fluid of high electrolytic strength the particle mobility (velocity) will be lower than for sols having a low electrolytic strength, since the particle charge is reduced by the adhering layer of strong counter-ions.

The classical equation normally used to calculate  $\zeta$ -potential<sup>9</sup> is:

$$\zeta = \frac{V_e \pi \eta}{4 \epsilon E} \text{ volts}$$

where:  $V_e$  = electrophoretic mobility in cm/sec

$E$  = applied field strength, volts/cm

$\epsilon$  = dielectric constant

$\eta$  = medium viscosity

This equation normally holds for particles whose size is large compared with the double layer thickness.

This picture of the "double layer" is further complicated by the "Stern layer" which is a very compact layer of the colloid's counterions that adhere to the particle surface with an electrostatic attraction that is greater than the thermal agitation forces that have removed other counter ions from the particle's surface and thereby created the particle charge. This is frequently considered to be a mono-layered



of ions exerting a linear reduction (with distance from the surface of the particle) on the charge potential. Immediately outboard from this layer is the bound solvent layer (bound to the particle) containing the diffused ions discussed previously, which with the unbound solvent and ions beyond the shear plane provide the diffuse double layer whose potential decays by a factor of  $1/e$  for a distance  $\delta$ , measured from the Stern layer into the solvent (see Figure 1). The thickness, or distance of the potential drop,  $\delta$ , can be calculated by the use of its reciprocal,  $\kappa$ , from the following equation:<sup>10</sup>

$$\kappa^2 = 1/\delta^2 = 8\pi n q^2 z^2 / \epsilon k T$$

where:  $n$  = number of ions per cubic centimeter

$q$  = electronic charge, esu-c.g.s. units

$z$  = valence of the ions

$\epsilon$  = dielectric constant of the solvent

$k$  = Boltzmann Constant,  $1.3804 \times 10^{-16}$  erg/deg. K

$T$  = temperature, degrees Kelvin

From this equation, the pH effect on  $\delta$  of the counter-ions can be calculated. For water at room temperature and monovalent ions at a 0.1 M solution, the double layer thickness,  $\delta$ , is approximately  $10^{-7}$  cm or 10  $\text{\AA}$ ; at 0.001 M the distance is 100  $\text{\AA}$ ; and at  $10^{-5}$  molarity the distance become 1000  $\text{\AA}$ . This further leads to the recognition that for spherical particles of radius,  $r$ , when  $\kappa r$  exceeds 10, the thickness of the double layer becomes one-tenth of the radius, and can be considered flat for most purposes. When  $\kappa r$  is  $< 10$ , the particle may be considered as a



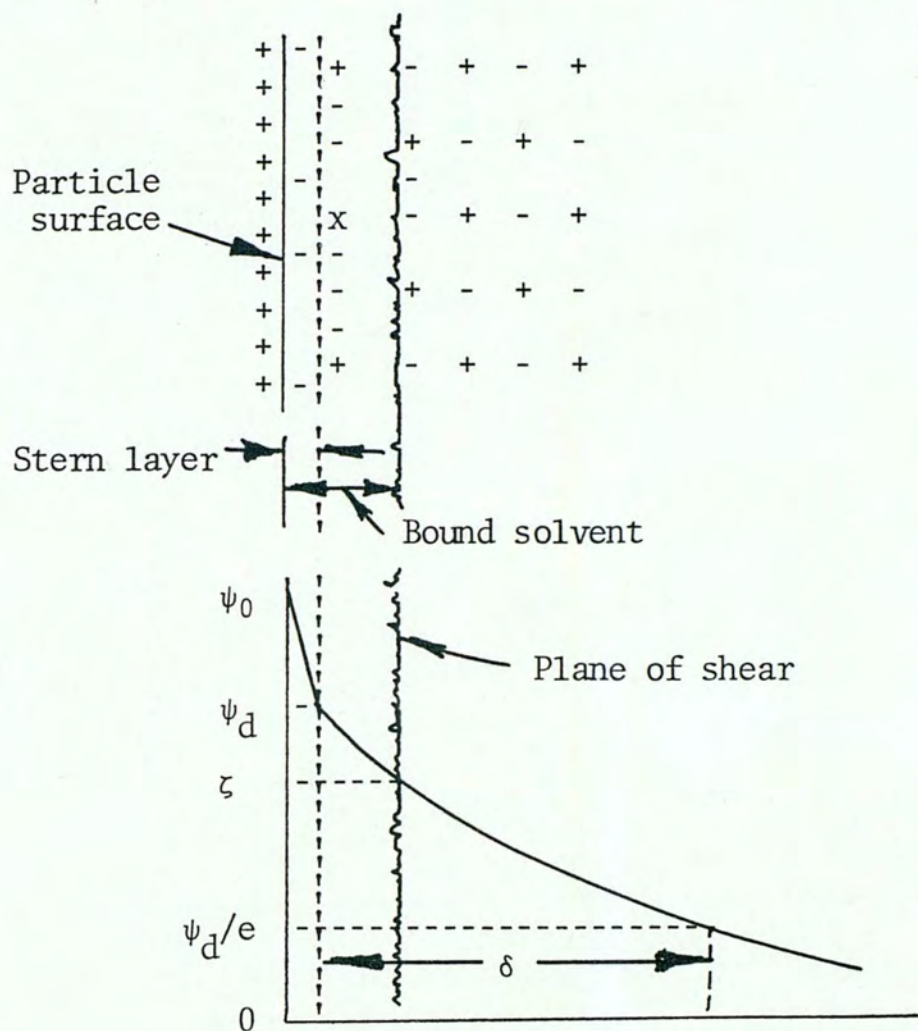


Fig. 1.<sup>8</sup> The structure of a double layer and the corresponding potentials.  $\psi_0$  is at the wall, the  $\psi_d$  at the beginning of the diffuse double layer,  $\zeta$  at the hydro-dynamic plane of shear. In the diffuse double layer the potential decays by a factor of  $1/e$  over a distance  $\delta = 1/\kappa$  for low potentials.



point charge\*. Flocculating agents frequently employ this pH effect by increasing the counterion electrolyte to the point that the field potential of the colloid charge has been reduced to zero (or a small value) and thereby removed the dispersive anti-coagulating repulsion created by like particle charges. On this basis, ferrous ions,  $\text{Fe}^{+3}$ , could therefore have a possible double advantage over other cations used to neutralize negatively charged particles in that they would more rapidly reduce the charge and double layer distance from the particle as well as provide a potentially ferromagnetic material in the double layer to assist coagulation with magnetic attraction between particles in a magnetic field.

Silica, silica minerals, tea-like organic colors, and most proteins show a negative charge normally when in a colloidal state in water with pH near 7. Various ionic forms of hydrous oxides of iron and aluminum are usually positively charged and tend to neutralize negatively charged colloidal particles and thereby reduce the particle charge and the zeta potential permitting greater coagulation.

Hydrophilic organic colloids (e.g. starches, proteins) have a high affinity for water (sometimes referred to as "lyophilic" - strong affinity between the dispersed phase and the dispersing medium) which tends to envelope the particle in a sheath of water molecules. These also form a barrier to coagulation of like particles. Thus the stability of the colloidal system composed of hydrophilic particles is governed by

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\* Mysels in Introduction to Colloid Chemistry, page 329, provides a table of electrolyte concentrations required below which the spherical shape of particles becomes important. Entry to the table is made using particle radius (from  $10$  to  $10^4 \text{ \AA}$ ) and valence of the counterions.



both charge and solvation, while for colloids having a hydrophobic characteristic (lyophobic) the stability depends primarily on the charge of the particle.

### C. Magnetic

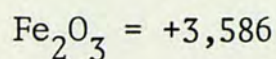
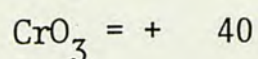
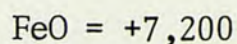
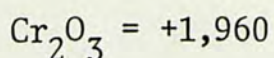
Based on a review of the CRC Handbook<sup>11</sup> and the fact that most organic compounds have only a magnetic-polarizability, and that this term acts to reduce the magnetic field in the material,<sup>12</sup> almost all organic colloids are diamagnetic\* and are not attracted or affected by a magnetic field. Actually diamagnetic compounds are repelled slightly by a magnetic field, but for practical purposes in water treatment processes such repulsion is negligible. Compounds containing certain transitional elements such as iron, manganese, cobalt, chromium and nickel (some of these in alloy or oxide form) are ferromagnetic, that is, they exhibit high magnetic properties at temperatures below a characteristic temperature called the Curie Point. It should be noted that the oxidation number or valence of the metal oxide has a bearing on its magnetic properties (due to variations in the number of unpaired electrons in the compound). As an example, the magnetic susceptibility in  $10^{-6}$  cgs units is:

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\* An applied magnetic field is reduced slightly within the material because of an alteration of the atomic electron orbits produced by the field. Diamagnetism is an atomic-scale consequence of the Lenz Law\*\* of induction. Permeability of diamagnetic materials is slightly less than that of empty space.

\*\* Lenz Law. When an electromotive force is induced in a conductor by any change in the relation between the conductor and the magnetic field, the direction of the electromotive force is such as to produce a current (or electron orbit orientation) whose magnetic field will oppose the change.





Paramagnetic materials are defined as those substances within which the magnetic induction is slightly greater than the applied magnetic field, i.e. the substance is attracted toward a magnetic field. Paramagnetism is considered to be caused principally by unpaired electrons in atoms, molecules, or ions. While the nucleus of atoms does exert some magnetic effects as can be utilized in NMR (nuclear magnetic resonance) analysis equipment the magnetic effects of unpaired electrons are approximately 1,000 times more pronounced.<sup>13</sup> While the magnetic property of a substance is a measure of the number, distribution and temperature of unpaired electrons in a particular particle, the relationship is complex involving the orbitals occupied by the molecule's or atom's electrons and there is currently no known formula by which magnetic characteristics of an element or compound can be estimated. However handbooks, such as the Chemical Rubber Company's (CRC) Handbook of Chemistry and Physics, carry extensive tables of the magnetic susceptibility of organic and inorganic materials. Ferromagnetic materials, that is, iron, cobalt and nickel, normally compound and alloy into materials of very high susceptibility. These ferromagnetic materials appear to be associated with unpaired electrons in the "3d" orbital as the outermost "shell"; a similar situation appears to occur with elements having 4f orbital unpaired electrons starting with atomic number 58 (Cerium) through number 66 (Dysprosium) in the rare earth series of the periodic table of elements.

In summary, colloids of interest in this paper are complex particles varying in composition, size, shape, density, and electrical and



magnetic physical characteristics. Composition has usually been confined to inorganic, organic compounds, and organic polymers (long-chain molecules with carbon atom backbone). Very recent developments of inorganic polymers (long-chain molecules with non-carbon, e.g. silicon, oxygen, sulfur, phosphorus, backbone) provide an entire new field of synthetics whose characteristics are still to be investigated.<sup>14</sup>

#### D. Colloidal Content in Water Systems

The character of colloidal particles in the influent of water and wastewater treatment plants varies greatly depending on location and water source. Colloidal dispersion of gas bubbles in water are of interest in treatment plants as they relate to foam and to aerobic treatment processes. For foam to form the colloidal gas must be hydrophilic, which results in the requirement that anti-foaming materials or processes must lead to reduction of the water surface tension. Normally the foam is air or dissolved oxygen, and in the case of wastewater treatment plants is usually an indication of soap and detergent concentrations present. It should be noted that gaseous oxygen,  $O_2$ , has a magnetic susceptibility of  $+3,449 \times 10^{-6}$  cgs units at  $20^\circ C$  but would not be expected to carry an electrical charge. Ozone on the other hand, could be expected to carry a negative charge but has a magnetic susceptibility of about  $7 \times 10^{-6}$  cgs at normal temperatures.

Colloidal dispersion of immiscible liquids in water normally require an emulsifying agent to maintain their stability. Such liquid colloids are mostly of organic origin, oil being a major emulsion of interest to water treatment processes. Soaps, synthetic detergents,



proteins, protein degradation products, egg yolk, lanolin, gum arabic, keolin, fuller's earth, colloidal clays and lampblack are examples of emulsifiers that can be found in waters having liquid colloids. While colloidal liquids can carry an electrical charge similar to a solid-phase organic colloidal material, the characteristics of the emulsifiers will normally be of greater concern. These emulsifiers, sometimes referred to as "association colloids" are normally hydrocarbon chain molecules that have both a hydrophilic and a hydrophobic extension. Micelles of these molecules form to stabilize the immiscible liquid colloidal suspensions with the hydrophobic extensions immersed in the liquid phase and the hydrophilic extension in contact with the surrounding water. Ions removed from the hydrophilic ends of the molecules tend to give the colloid liquid its electrical characteristics and normally negative charge. The molecules of the emulsifiers being hydrocarbons and of an organic origin normally, are diamagnetic and do not exhibit magnetic properties.

While the amount, composition, and types of colloidal material found in waters are many and varied, the history and source of a water can provide a guide to what may be expected in a particular situation. Rain water will have colloidal material that has been washed from the air or that provided the particulate matter upon which the water vapor initially condensed. Dusts obtained from wind action and erosion on land surfaces as well as residues from wave spray on the oceans, soot and other manmade emissions, and volcanic eruptions are the chief sources for entrapped particles in rainwater.



Uncontaminated ground waters will normally contain clays and mineral colloidal particle matter. Most clays are a form of hydrous silicates of aluminum such as kaolin. Magnesium silicates (talc), compounds and oxides of iron and various carbonates can also be expected in ground waters. Organic matter is minimal in uncontaminated ground waters and will consist primarily of fossil residue and anaerobic or chemically reduced organic materials. Except for some industrial waste waters from mineral processing activities, ground waters would have the greatest probability of containing colloidal matter susceptible to magnetic processing treatment.

Organic colloidal matter stemming from plants and animal wastes such as proteins (polyaminoacids), starches and cellulose (straight chained polysaccharides), and other polysaccharide and hydrocarbon chains are the most commonly occurring naturally formed colloids found in surface waters. Inorganic colloids in surface waters originate from material picked up by stream flow erosion such as bentonite and other clay particles. Manmade or synthetic colloids found in surface waters can be classified into three categories:<sup>15</sup> the association colloids, such as detergents, that associate spontaneously into colloid particles with the hydrophobic portion of the molecules grouping together or in an immiscible liquid particle; polymerization of large molecules either by condensation or by addition into colloidal particles; and diuturnal colloids which are tiny crystals or droplets formed from a bulk phase either by grinding or milling, or (more frequently) by chemical precipitation or vapor condensation of an insoluble material that tends to disperse



throughout the medium when in a finally divided form. Sulfur and gold are examples of diuturnal colloids.

Colloidal content of a domestic originated wastewater and its effluent from an activated sludge secondary treatment plant was investigated and reported by Rickert and Hunter.<sup>16</sup> By sedimentation and centrifuge processes, they were able to approximate the size fractions for settleable ( $>1000\mu$ ), supracolloidal ( $1 - 100\mu$ ), colloidal ( $0.05 - 1\mu$ ), and soluble matter. The concentrations of volatile solids (VS), total organic carbon (TOC), chemical oxygen demand (COD), turbidity, and inorganic matter for each sized fraction were determined (see Table 1). It is considered significant that all concentration show colloidal matter to provide the lowest parameter concentrations and lowest parametric percentage of total parametric content. The turbidity measurement was taken as an indication of the number, size, and shape of the constituent particles. However, it was known that shapes differed after treatment and it was suspected that the size distribution also changed with the treatment, thus the authors could not conclude that the number of colloidal particles decreased with treatment in spite of the large decrease in Jackson turbidity units. The nature of the colloidal particles was reported as follows:

"Electron micrograph studies have shown that bacterial cell walls and cellular debris are the dominant forms of colloidal matter in secondary effluents. Viruses (virus particles range in diameter from 200 to 3,000  $\text{\AA}$  and consist typically of a protein coat or capsid<sup>18</sup>), phages, and detached flagella are present to a lesser degree . . . In contrast, the colloidal matter in raw wastewater is largely composed of irregularly shaped, comparatively thick, fluffy-looking particles, which appear to be of nonbacterial origin."



TABLE 1

TURBIDITY AND PARAMETRIC CONCENTRATIONS IN WASTEWATER AND SECONDARY EFFLUENTS<sup>17</sup>

Substance	Fraction	Turbidity		VS		TOC		COD		Inorganic	
		JTU	% Total	mg/l	% Total	mg/l	% Total	mg/l	% Total	mg/l	% Total
Wastewater	Soluble	7.0	12	116	48	46.0	42	168	40	235	86
	Colloidal	13.0	23	23	9	12.0	11	43	10	8	3
	Supracolloidal	24.5	44	43	18	22.0	20	87	21	14	5
	Settleable	11.5	21	59	25	29.0	27	120	29	15	6
	TOTAL	56.0	100	241	100	109	100	418	100	272	100
Secondary Effluent	Soluble	0.8	9	62	67	16.5	69	46	74	250	97
	Colloidal	2.0	23	6	7	1.5	6	3	5	2	1
	Supracolloidal	5.9	68	24	26	6.0	25	13	21	4	2
	Settleable	0.0	0	0	0	0.0	0	0	0	0	0
	TOTAL	8.7	100	92	100	24.0	100	62	100	256	100



The article concludes that secondary wastewater treatment will normally decrease colloidal concentrations of organic and inorganic materials and that they form a small proportion of the total solids in the secondary effluent. Further it was concluded that the chemical evidence indicated the effluent colloidal matter was formed during the biological treatment rather than influent colloidal materials that were unaffected by the treatment process. The fouling of ion exchange resins and electrodialysis membranes that had been associated with the presence of colloidal matter in biologically treated effluents were therefore considered to reflect the nature of the materials rather than an increased quantity of colloidal matter resulting from the biological treatment process.



### CHAPTER III

#### ELECTRIC AND MAGNETIC FIELD THEORY

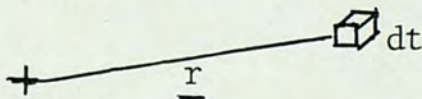
Electric and magnetic field theory are similar and parallel in nature although one is the result of a static charge of electricity while the other results from a flow of electricity or movement of the electrical charge. The mathematical models developed to represent these fields are based upon experimental results of macro-systems that can be measured and not upon quantum mechanics involving the electron/proton distribution in the molecules due to the complexities of such systems. The following development was obtained from a physical chemistry text by Barrow.<sup>19</sup>

#### A. Electric Field Theory

The dipole moment,  $\mu$ , of two equal and opposite charges within a molecule is defined as the product of the charges and the distance between them:

$$\mu = qr \quad \text{where: } q = \text{charge quantity and } r = \text{distance between the positive and negative charge.}$$

Letting  $\Psi(r)$  represent the charge density at a position defined by the vector,  $\underline{r}$ , and  $t$  represent a volume element:



$$\text{then: } \mu = \int \Psi(r) \underline{r} \, dt$$

Molecular dipole moments are normally expressed in units called the "debye" =  $10^{-18}$  esu-cm. The charge of an electron,  $4.80 \times 10^{-10}$ , at a distance  $r$  of 1 Angstrom unit thus gives a dipole moment:



$$\mu = (4.8 \times 10^{-10})(1 \times 10^{-8}) = 4.80 \times 10^{-18} \text{ esu-cm} = 4.8 \text{ debye}$$

An induced dipole moment is created when an electric field is applied to a material and the molecular charge distribution is distorted. This polarizability of a molecule is determined by the strength of the electric field required to achieve a given level of polarity (dipole moment) for the molecule. Polarizability is defined as the dipole moment induced by a unit electric field. Thus all molecules are polarizable and can have an induced dipole moment even though their "permanent" or normal dipole moment is zero.<sup>21</sup>

The similarity of electrical fields to those of gravity and magnetic fields, is best exemplified in Coulomb's law giving the interaction force,  $f$ , of stationary charges of strength  $q_1$  and  $q_2$  when separated by a distance,  $r$ , in a vacuum (dielectric constant = 1) as:

$$f = \frac{q_1 q_2}{r^2}$$

where:  $f$  = force in dynes

$q_x$  = point charge in esu

$r$  = distance in cm.

The convention has been chosen that:

$f$  is positive, (+), when the charges have the same sign (repel)

$f$  is negative, (-), when the charges have different signs (attract)

By use of this formula the basic electrical charge and force units have been defined, to wit:

An esu charge repels an equal charge placed 1 cm away with a force of 1 dyne

1 coulomb =  $3 \times 10^9$  esu (normal unit of charge used)



The electric field intensity,  $\underline{E}$ , is a vector quantity having direction and magnitude and is measured in dynes/esu, or:

$$\underline{E} = \frac{f}{q}$$

Thus for a sphere of radius,  $r$ , the intensity is  $q/r^2$ , and the total lines of force emanating from a charge are:

$$q(4\pi r^2)/r^2 = 4\pi q$$

Thus an electric field of unit positive charge is represented by  $4\pi$  lines of force.

A unit positive charge in an electric field of  $\underline{E}$  intensity has a force of  $E$  dynes acting on it. The change in potential energy of the charge when moved a distance,  $dr$ , toward the positively charged pole generating the field is equivalent to performing work, i.e. a force times a distance. Therefore, the change in potential energy,  $dV = -E dr$  or  $E = -dV/dr$ . The unit of potential difference is defined as a volt and is equal to  $1/300$  esu units.

For a condenser having a plate area,  $A$  in  $\text{cm}^2$ , the cathode and anode plates being separated by a distance,  $d$ , we obtain  $E = V/d$ . With a plate charge density,  $\sigma = q/A$  charges/ $\text{cm}^2$ , we will obtain  $4\pi\sigma$  lines of force/ $\text{cm}^2$  and  $E = 4\pi\sigma$  dynes/esu since one line of force per square centimeter corresponds to a unit field. Assuming no attenuation from vacuum or air between the plates, the capacitance of a condenser,  $C_o = q/V$ , which is the charge held on the plates per unit potential. Since,

$$q = \sigma A \quad \text{and} \quad V = Ed = 4\pi\sigma d,$$

then,

$$C_o = \frac{\sigma A}{4\pi\sigma d} = \frac{A}{4\pi d}$$



Dielectric material between condenser plates is non-conducting and alters the above relationship to reduce the force acting on the charges (attenuated) to:

$$f = q_1 q_2 / \epsilon r^2$$

where:  $\epsilon$ , the dielectric constant, varies with the medium and temperature. Thus the electric field intensity is  $E = 4\pi q / \epsilon$  lines of force/unit charge, the applied voltage,  $V = 4\pi o d / \epsilon$ , and the capacitance,  $C = \epsilon A / 4\pi d$ . Thus by measuring the capacitance of a given condenser with and without dielectric material between the plates a value for the dielectric constant can be obtained,  $\epsilon = C / C_0$ , and it can be seen that the capacitance is increased by the dielectric material. (For distilled water at  $20^\circ\text{C}$ ,  $\epsilon =$  approximately 80.0)

The mechanism by which dielectric material decreases the electric field between condenser plates can be developed by supposing the material is polarized by the electrical field and designating the induced dipole moment,  $p$ , as the moment developed in a cubic centimeter of material by the field (for water  $p = 1.87 \times 10^{-18}$  esu). The induced dipole moment in the dielectric material tends to balance the charges on the condenser plates and thereby reduce the electric field. If we define the field intensity between the plates without dielectric material as:

$$E_0 = 4\pi\sigma$$

then,

$$E = 4\pi(\sigma - p) = E_0 - 4\pi p = 4\pi p / (\epsilon - 1).$$

This gives us the electric field in a dielectric medium in terms of polarization of the dielectric and the dielectric constant.



Barrow<sup>21</sup> then develops the Clausius-Mosotti equation that permits the calculation of either the polarizability of a molecule,  $\alpha$ , or the molar distortion polarization,  $P$ , from measurements of the dielectric constant of the material.

$$P = (4/3)\pi N\alpha = (\epsilon - 1) M/\rho (\epsilon + 2)$$

where:  $P$  = molar distortion polarization

$N$  = Avogadro's constant =  $6.0225 \times 10^{23} \text{ mole}^{-1}$

$\alpha$  = proportionality constant when the induced dipole is proportional to the field acting on the molecule

$\epsilon$  = dielectric constant

$M$  = molecular weight of dielectric

$\rho$  = density

When the dielectric material has a permanent dipole moment,  $\mu$ , the effect on  $P$  and  $\alpha$  is expressed in the Debye equation:

$$P = (\epsilon - 1) M/\rho (\epsilon + 2) = (4/3)\pi N (\alpha + \mu^2/3kT)$$

where:  $\mu$  = permanent dipole moment of the material molecules

$k$  = Boltzmann constant =  $1.3805 \times 10^{-16} \text{ erg/degree}$

$T$  = temperature, degrees Kelvin

The polarizability,  $\alpha = \mu_{\text{induced}}/E_{\text{internal}}$ ,

where:  $\mu_{\text{induced}}$  = induced dipole moment

$E_{\text{internal}}$  = electrical field in the molecule

$\alpha$  = proportionality constant

To determine  $\alpha$  and  $\mu$  we can either: (1) Measure  $\epsilon$  and  $\rho$  as functions of temperature, then a plot of  $M(\epsilon-1)/\rho(\epsilon+2)$  against  $1/T$  giving a straight line whose slope =  $\mu$ , and the line intercept with the  $1/T=0$  axis is the value of  $\alpha$ ; or (2) If  $\mu = 0$  the  $\epsilon = n_R^2$  where  $n_R$  is the refractive



index of the material, then solving for  $\alpha$  we obtain:

$$\alpha = (3/4\pi N) (M) (n_R^2 - 1)/\rho(n_R^2 + 2)$$

Substituting the values of  $\alpha$  and  $\epsilon$  into the Debye equation, a value of  $\mu$  can be obtained.

Percentage ionic character is a measure of  $\mu_{\text{observed}}$  to  $\mu_{\text{calculated}}$  where  $\mu_{\text{calculated}}$  assumes the bonding electrons are held by the negative atom and the bond length is the distance between the charges, e.g.

$$\text{HCl bond length} = 1.275\text{\AA}, \mu_{\text{obs}} = 1.03$$

$$\mu_{\text{ionic}}(100\%) = (4.8 \times 10^{-10} \text{ esu})(1.275 \times 10^{-8} \text{ cm}) = 6.11 \text{ debyes}$$

$$\% \text{ ionic character} = (1.03/6.11) \times 100 = 17\%.$$

In general it has been found that the greater the difference in electronegativity between bound atoms in a molecule, the greater the dipole moment. Water has been found to have a dipole (bond) moment of 1.85 debyes, other compounds are listed in CRC<sup>22</sup> tables on pages E-69 to E-72.

## B. Magnetic Field Theory

Practical applications of magnetic phenomena have been less than those involved with electrical fields, primarily because of the lack of strong magnetic properties in most compounds, although, similar to electric fields, all materials do provide a response, positive or negatively, to a magnetic field. Magnetism is defined as a phenomena exhibited by a force field produced by a magnet or by an electric current. Similar to gravity forces, we currently do not understand the basic cause or composition of such fields. However, there does exist a very solid and factual relationship expressable in mathematical equations between elec-



trical and magnetic phenomena. In terms of relativity, it is noted that an electrical current would exhibit no magnetic properties if the observer were moving at the same velocity as the electron flow of electrical current, although two parallel conductors with identical electron flow would exhibit repulsive reactions to each other. Repulsion of like static electrical charges might thereby be considered a magnetic phenomena where we, the observers, are moving at the electron flow velocity. This analogy becomes difficult to relate to materials possessing paramagnetic and diamagnetic properties although the counterpart appears to be electrical conductivity and dielectric properties.

Similar to electrical polarizability,  $\alpha$ , and the dipole moment,  $\mu$ , the magnetic counter parts are identified as magnetic polarizability,  $\alpha_M$ , and magnetic moment,  $\mu_M$ . The magnetization per mole induced by unit magnetic field strength is defined as the molar magnetic susceptibility,  $\chi_M$ . Mathematical model symbols and relationships are presented below.

B denotes the magnetic field in a material, gauss, or Maxwell units.

H is the magnetic field intensity in a vacuum measured in terms of the force on a unit magnetic pole, oersted or gilbert units.

I is the intensity of magnetization, represents the magnetic moment per unit volume of material (can be either positive or negative) in amperes.

These quantities are related by the expression:

$$B = H + 4\pi I$$

For chemical convenience, the intensity of magnetization per unit field strength, i.e.  $I/H$  is multiplied by  $M$  (the molecular weight)/ $\rho$  (material density) to provide values in molar quantities, thus:



$$\chi_M = \frac{M}{\rho H} = N \left( \alpha_M + \frac{\mu_M^2}{3kT} \right)$$

Most organic compounds have a zero magnetic moment,  $\mu_M^{23}$  and the magnetic-polarizable contribution,  $\alpha_M$ , tends to reduce the magnetic field, i.e.  $\alpha_M$  is negative. These compounds have all their electrons paired and, as a result, attenuate the magnetic field within the material. In these cases  $\chi_M$ ,  $\alpha_M$  and  $I$  have negative values and the material is said to be diamagnetic. Diamagnetic substances are repelled by a magnetic field, and the induced magnetic moments are balanced within the substance. The magnetic characteristics of all atoms, molecules, or ions result primarily from the spin of electrons. It is for this reason that the magnetic property of a material is a measure of the number and distribution of unpaired electrons in a particular particle. In diamagnetic materials, the magnetic effect of an individual electron is balanced by another electron with opposite spin, as in orbitals where two electrons have opposing spins. Hall and Keyworth<sup>24</sup> point out that substances that are diamagnetic belong to one of the following categories:

1. All noble gases and ions with noble gas configurations, such as  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{++}$ ,  $\text{Sc}^{+++}$ , and  $\text{O}^{--}$ .
2. All ions that, in addition to (1), have completely filled "d" or "f" orbitals.
3. All particles that contain a pair of "s" orbital electrons in addition to a noble gas core (for example -  $\text{Be}$ ,  $\text{Zn}$ ,  $\text{Ga}^+$ , and  $\text{Pb}^{++}$ ).
4. All covalent substances that have no unpaired electrons. This includes practically all covalent compounds. Exceptions include a few odd-electron molecules, such as  $\text{NO}$  and  $\text{NO}_2$ , free radicals, such as  $\text{CH}_3$ , and perhaps the simplest of all, the diatomic oxygen molecule,  $\text{O}_2$ .



Paramagnetic materials, on the other hand, are those within which an applied magnetic field is slightly increased by the alignment of electron orbits, i.e.  $\alpha_M$  has a positive value when there is no magnetic moment in the material, or, the magnetic moment existing in the material is greater than the negatively valued polarizability term,  $\alpha_M$ , which is more generally the situation for paramagnetic materials. Using classical treatment and Ampere's law that current flowing in a coil will produce a magnetic field perpendicular to the coil, and then treating an electron in orbit as the current flow, it can be shown that the ratio of the magnetic moment to the orbital angular momentum is equal to the electron charge,  $e$ , divided by  $2mc$ , where:

$$m_e = \text{electron rest mass} = 0.9109 \times 10^{-27} \text{ g}$$

$$c = \text{speed of light} = 2.9979 \times 10^{10} \text{ cm/sec}$$

$$h = \text{Planck constant} = 6.6256 \times 10^{-27} \text{ erg-sec}$$

i.e.  $\mu_M/m_e v r = e/2m_e c$ . The angular momentum of an electron depends on the quantum number,  $l$ , and has the value,  $\sqrt{l(l+1)} (h/2\pi)$ . Therefore, the magnetic moment due to orbital motion of an electron is:

$$\mu_M = \frac{eh}{4\pi m_e c} \sqrt{l(l+1)}$$

Magnetic moments of substances (atoms, ions, or molecules) are normally expressed in Bohr magnetrons,

$$\text{B.A.} = \frac{eh}{4\pi m_e c} = \mu_0 = 0.9273 \times 10^{-20} \text{ erg/gauss}$$

While this expression for magnetic moment appears to hold for free atoms, the formula does not hold in atomic and polyatomic ions in solution, and it is thought that the failure of the orbitals to line up with the applied



magnetic field is prevented by the nuclear configuration of the molecule or the solvating molecules in the case of ionic solutions. Thus the orbital-magnetic-moment contribution to the magnetic susceptibility is generally quite small.

As a result of the inability to correlate orbital electron contributions to measured magnetic moments of polyatomic and ionic materials, it has been found that a high correlation can be obtained on the basis the angular momentum associated with the spin (on its own axis) of an unpaired electron\*.

The relationship between the magnetic moment and the number of unpaired electrons,  $n$ , has been shown from atomic spectral data to be:

$$\mu = \sqrt{n(n + 2)} \quad \text{in Bohr magnetrons or,}$$

$$\chi_M = \frac{\mu_0^2}{3kT} N n(n + 2) \quad \text{magnetic susceptibility in cgs units}$$

Experimental data have tended to confirm these equations as indicated in the table on the following page. However, the main use of these formulae have been to indicate to the investigator the probable electron structure configuration of transition elements in ionic complexes or molecules.

Now turning to some more common magnetic terms and formulae applicable to macro systems (see Appendix II for units and conversion factors) we find that magnetic induction,  $B$ , is the resulting magnetic flux or field density in a substance that is subjected to a magnetic

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\* When electrons have been paired in orbit they have opposing spin and therefore the pair's resultant magnetic moment is zero. It is thought probable by the author that the reason an electron entering an orbit with another electron having similar spin will "flip" its axis to obtain opposite spin is the result of the magnetic fields of the two electrons.



TABLE 2

Ion	Number Unpaired Electrons	Calc. $\mu$ B.M.	Exp. $\mu$ B.M.	$\chi$ at 25°C
K <sup>+</sup>	0	0	0	0
Cu <sup>++</sup>	1	1.73	1.7-2.2	1,260 x 10 <sup>-6</sup>
Ni <sup>++</sup>	2	2.83	2.8-4.0	3,360 x 10 <sup>-6</sup>
Cr <sup>+++</sup>	3	3.87	~3.8	6,290 x 10 <sup>-6</sup>
Co <sup>+++</sup>	4	4.90	~5.4	10,100 x 10 <sup>-6</sup>
Fe <sup>+++</sup>	5	5.92	~5.9	14,700 x 10 <sup>-6</sup>



field,  $H$ . The magnetic permeability,  $\nu$ , is the coefficient for the material which when applied to the magnetic field intensity gives the induced magnetism in the substance, i.e.:

$$B = \nu H = H + 4\pi I$$

The magnetic susceptibility,  $\kappa$ , equals  $I/H$  and thus  $\nu = 1 + 4\pi\kappa$ . The magnetizing force (magnetic field intensity),  $I$ , is measured by the force acting on a unit pole,  $m$ . The unit field intensity, the oersted, is that field which exerts a force of 1 dyne on a unit magnetic pole. The field intensity can also be specified by the number of lines of force intersecting a unit area normal to the field. The unit magnetizing force is measured by the space rate of change (variation) of magnetic potential, normally in Gilberts per centimeter.

The total magnetic flux through an area perpendicular to the magnetic field is a product of the area and the field strength (intensity). The units of induced flux are normally measured in terms of lines, maxwells, volt-seconds, or Webers. The units of magnetic flux density in the material are then measured in Gauss which represent one maxwell per square centimeter density.

Magnetic potential (magnetomotive force) is the magnetic counterpart of the electrical potential, the volt, and is similarly defined as the work required to bring a unit positive pole from an infinite distance (zero potential) to the point. The unit is the "gilbert" which represents an erg of work required to move a unit magnetic pole from one point to another, and is equal to  $10/4\pi$  ampere-turns. The unit pole is defined as the quantity of magnetis,  $M$ , which when concentrated at a



point 1 cm from a similar quantity in a vacuum will be repelled by a force of 1 dyne. The Gauss can also be defined as the magnetic flux density required to produce an induced electromotive force of 1 abvolt in a 1 cm long conductor moving at 1 cm/sec through the field and at right angles to the field ( $1 \text{ abvolt} = 1 \times 10^{-8} \text{ volts}$ ).

The force between two magnetic poles can be represented by  $F = \frac{mm'}{r^2}$  where  $F$  is dynes,  $r$  is in cm, and  $m$  and  $m'$  are in unit pole strengths.

Ferromagnetic is a relatively loose term that is applied to materials and substances having an abnormally high magnetic permeability a definite saturation point, and exhibit appreciable residual magnetism and hysteresis. All ferromagnetic substances have a definite temperature at which they lose their ferromagnetic characteristics and revert to a paramagnetic material. This temperature is known as the Curie Point and is usually lower than the melting point (this is probably the result of increasing the energy in the unpaired electrons to raise them into higher orbitals in which they become paired). It is considered likely that at temperatures below the Curie Point, the magnetic moments are parallel aligned by interaction between the material molecules in a zero magnetic field. The Curie Point for iron, Fe, is  $770^{\circ}\text{C}$ ; for cobalt, Co -  $1131^{\circ}\text{C}$ ; for nickel, Ni -  $358^{\circ}\text{C}$ ; and for gadolinium, Gd -  $16^{\circ}\text{C}$ .

There are some materials which exhibit "antiferromagnetic" characteristics wherein the magnetic moments of atoms or ions tend to assume an ordered arrangement of alternate polarity in a zero applied field, such that the vector sum of the moments is zero when below a



"Neel Point" temperature, above this temperature the material becomes paramagnetic. A related term, "ferrimagnetic" refers to materials in which the magnetic moments assume an ordered, but non-parallel, arrangement in zero field, again at temperatures below the Neel Point, above which they become paramagnetic. In this case different "domains" within the material appear to develop non-parallel (to other domains) magnetic moments, the macroscopic behavior results in a material having magnetic moments and susceptibility lying somewhere between ferromagnetic and paramagnetic when at temperatures below the Neel Point.

Depolarization of ferromagnetic particles is frequently necessary in practical applications of magnetic techniques and processes for purposes of more efficient dispersions, classification, and screening as well as decreasing moisture content in filter cake and improved separation selectivity. The Eriez Magnetics company has developed the following empirical equations that permit one to calculate the major parameters of a demagnetising coil design for magnetite suspensions in a water medium:

$$L = \frac{0.2(a + c)^2 N^2}{(3a + 9b + 13c) 10^6} \quad \text{Henries of Inductance}$$

$$H = \frac{0.495 NI}{\sqrt{(a + c)^2 + b^2}} \quad \text{rms oersteds, field strength}$$

where: a = inside diameter of winding

b = length of coil

c = radial depth of winding

N = number of turns

I = coil current



NOTE: About 450 rms oersteds at 60 cycles is normally sufficient for depolarization of natural magnetite under ordinary conditions. An alternate method for depolarization of the colloidal material is to heat it to a temperature above the Curie point and permit to cool under zero magnetic field conditions.



## CHAPTER IV

### COLLOID REACTIONS IN ELECTRIC FIELDS

The term "electrophoresis" (sometimes called "cataphoresis," or "electrokinetics") was originally introduced to mean the migration of charged colloidal particles in an electric field and will be so treated in this paper, although there has been a tendency to expand the definition to cover charged particles smaller than a colloidal particle and ions in solution. However because such charged particles normally have "entrapped" ions in the electrical double layer surrounding the particle, it must be recognized that electrophoresis is intimately connected with the ionic part of the electrical double layer, and involves understanding and consideration of the electrical double layer. The reduced particle potential resulting from the entrapped "counterions" in the double layer become a part of the solid or liquid phase as the particle moves tangentially with respect to the surrounding medium. A brief history and summation of Dr. McLellon's collected papers dealing with electrophoresis assists in an understanding of the phenomenon.

Kruyt<sup>25</sup> starts his history of the colloid science with F. Selmi (1845 and later) and his recognition of solutions containing dispersions coarser than molecular. Th. Graham (1861) introduced the word "colloid" as defining a non-crystalline solid having a characteristic slow diffusion rate in a "sol" medium. C. von Nageli (1858 and later) introduced the concept of "micelle," a polymolecular aggregate with an internal crystal structure. J. M. Van Bemmelen (1877 and later) is credited with



the introduction of boundary surface phenomena and the principle of adsorption. By 1908 (with thanks to J. Perrin for his atomic structure investigations) it became generally recognized that colloids were a dispersion - subject to Brownian motion - and that they were intermediate between molecular dispersions and that of coarse suspensions. Initially polymolecular aggregates having a large boundary surface between system phases and slow diffusion characteristics were defined as colloidal, however, with the advent of polymerization of organic compounds, it became recognized in the early part of this century that biocolloids having single large molecules dispersed in solution also had "colloidal" characteristics. (With recent advances in inorganic polymerization, the polymolecular concept of a colloid particle will become even less acceptable.)

Colloids were and, occasionally in references today, are termed suspensoids, hydrophobic, lyophobic, inorganic, irreversible and insoluble colloids that are very sensitive to small amounts of electrolyte. Further, the influence of flocculating salts normally depends on the valency of the counterions more than would normally be expected by a proportionality factor of the valency. By the early 1900's the electrophoretic mobility and electrokinetic characteristics of these particles were recognized and were being measured. It was found that organic colloids or biocolloids behaved differently from inorganic colloid in that large concentrations of electrolytes are required to obtain similar electrical behavior and was attributed to an interaction, hydration, or solvation, between the organic particle and the medium or substrate. From a physical chemistry standpoint these colloid systems



showed little osmotic pressure, no rise in the boiling point or lowering of the freezing point and the ionic conductivity of the electrolyte solutions appeared to show no analogy to the unidirectional electrophoresis of the colloids.

Irving Langmuir<sup>26</sup> presented a very interesting paper on the state-of-the-knowledge of adsorption forces in 1938 as the Seventeenth Faraday Lecture. The paper discusses chemical forces (covalent bonds) which depend upon the nature of the joined atoms with these forces coming into being at very short ranges in the order of the radii of atoms or about  $1 \text{ \AA}$ . Van der Waals forces acting between molecules are considered as "non-specific forces which result from the mutual interactions of electronic shells." A third force, the repulsive forces which prevent the interpenetration of electronic shells is mentioned but not discussed. All of these forces are considered by Langmuir to be electrical in nature although the chemist normally associates the forces with quantum phenomena. (No consideration is given in this paper - or for that matter, in most of the technical literature available - to magnetic and gravitational forces that may exist at the atomic and subatomic level.) Using Coulomb's law, Langmuir shows that significant forces in the structure of matter correspond to potential energies of the order of  $kT$  (about 0.025 electron volts at room temperature), which is a measure of the energy of thermal agitation. Using the Coulomb law it is possible to estimate the distances within which such forces may be significant. Thus the potential energy between two electrons is equal to  $kT$  when the distance between them is  $560 \text{ \AA}$  (in a



vacuum). In water with a dielectric constant of 80, the distance is only  $7 \text{ \AA}$ . With multivalent ions and particularly with large colloidal particles, the effective distances, which increase in proportion to the charges on the interacting particles, may become relatively great. Colloids whose micelles carry charges of 10 or more units may show effective ranges of several hundred or even several thousand Angstrom units.

The dipole moment of liquid molecules provides the dielectric characteristics of a substance and these dipoles can be oriented by external fields, local fields, ions, or other dipoles. The interaction between a dipole and an ion gives a force which varies with the inverse cube of the distance and depends on the orientation of the dipole. Molecules of water having a dipole moment = 1.87 Debye units (1 Debye unit =  $10^{-18}$  cgs units), should theoretically require a field of the order of  $10^7$  volts/cm to orient the majority of the dipoles against the effect of thermal agitation. A field of this magnitude would exist at a distance =  $12\epsilon^{-1/2} \text{ \AA}$  from a univalent ion, where  $\epsilon$  = dielectric constant. Thus for water with a constant of 80, the distance would be approximately  $1.3 \text{ \AA}$ .

A single layer of completely oriented water molecules on a plane surface would give a double layer potential of approximately 15 volts if the dipole moment remained at 1.87 debye units. However, dipole molecules, when completely oriented exert forces on one another which vary with the inverse fourth power of the distance. Under conditions that give incomplete orientation, the force is proportional to



the inverse seventh power. Only when the dipoles are practically in contact can energies be comparable with  $kT$ .

Langmuir continues his molecular description by pointing out that van der Waals forces between non-polar molecules vary as the inverse seventh power of the distance and are thus less effective (for agglomeration purposes) than the dipole forces. Covalent bonding forces and repulsive forces due to the "impenetrability" of electronic shells were considered by Langmuir to have extremely short ranges of action of the order of  $1 \text{ \AA}$  or less.

The period from the late forties to present has seen a rapid expansion of knowledge and instrumentation capability in the field of electrophoresis. While some of the effort was directed to research involving inorganic substances, such as Voet<sup>27</sup> who was interested in pigment dispersions in organic liquids having a low dielectric constant (since he worked for an ink company), the majority of effort has been in the fields of biochemistry and molecular biology where electrophoresis has become an essential laboratory and clinical tool for micro-analysis of proteins, nucleic acids, enzymes, antigens and other colloidal particles found in organic fluids. In this area the field has become so extensive and diversified there is not general agreement and acceptance of the meaning of such terms as:<sup>28</sup> "Moving boundary electrophoresis" - this is similar to chromatography and the movement of the colloidal particles in a fluid column due to the presence of an electrical field; "Zone electrophoresis" - the colloidal particles are separated into layers or "zones" by a voltage gradient; "Isotacho-



phoresis" - a form of steady-state separation or displacement of particles having different electrophoretic characteristics; "disc electrophoresis" - a combination of concentration of sample components in large pore spacer gels, a molecular sieving by which individual molecules are electrophoretically separated on the basis of their size (molecular weight) and shape or tertiary structure, and the electrocharge effect by which the sample molecules are fractionated according to their net electric charge; "Isoelectric focusing" - by providing a pH gradient in a fluid column in an electrical field the charged colloidal particles will tend to "layer" at a particular pH.

In summary one can state that there has been considerable advance, especially since the end of World War II, in the knowledge and control of colloidal particles in an electric field with most of the work performed in the biochemical and medical field due primarily to the high colloidal content of blood and animal serums. Electrophoresis is a complex subject today since it is basically the study of a relationship between many physical and electrical parameters such as:

- a. Particle parameters which are: size, shape, concentration, electrical charge, degree of hydration, and dissociation.
- b. Medium parameters which are: viscosity, pH value, temperature, and ionic strength.
- c. Electrical field strength and migration time or exposure to the field.

Applications of the science of electrophoresis has been confined chiefly to the laboratory for research and analysis purposes. Its employment for large scale pollution controls appears extremely



limited at the present state of the science, although it could enhance the environmental engineer's understanding of colloidal characteristics, flocculating and dispersion characteristics of polymers and chemicals on colloidal suspensions. A reaction reported by Clemens and Ziemba<sup>29</sup>, more electrolytic than electrophoretic in nature, resulted in improved liquid waste treatment at the Swift Edible Oil Co. Refinery in Bradley, Illinois. A 95% recovery of inedible oil and fatty material (approximately 7,000 pounds per day) was reported with an accompanying reduction in BOD, fats and suspended solids of 80-90% through use of polyelectrolytes ( $10-12 \times 10^6$  mol. wt. Swift Chemical Co. X400) and a skim tank and flotation tank equipped with immersed anodes (the tank surface forming the cathode). Using an acid to bring the pH to 4.5 - 5.5, 20% alum and 0.2% polyelectrolyte and a d.c. current, the effluent was suitable for wasting to sewage, a small sludge residue to land fill, and the recovered inedible fats had a commercial value.

Similar to environmental sciences, due to the complexities of each situation, an empirical approach is necessary although formulae for basic relationships have been established. A hypothetical example of the use of electrophoresis has been developed in Appendix I to obtain an appreciation for the magnitude of the forces and velocities one could expect employing this method for tertiary treatment to remove a colloidal suspension not amenable to removal by primary and secondary treatments. This example assumes electrophoretic characteristics similar to a protein and a 50,000 gallon per day facility and develops a facility having two 6 feet x 7 feet electrode plates forming the sides of a channel



and spaced either two or four cm apart would concentrate charged particles in portions of the stream adjacent to the plate having an opposite charge to the particle. ---

Now if we were to impress a magnetic field at right angles to the electrical field discussed here and also at right angles to the stream flow and properly oriented pole-wise to support the electrophoretic movement direction of the colloid particles, the removal of such charged particles might be further enhanced. With this in mind, literature on colloidal reactions to magnetic fields was researched in the following chapter.

It should be noted that if high voltage fields are utilized for water treatment, a bonus can be obtained by the disinfectant action of the field on various species of bacteria and yeasts. It has been determined<sup>30</sup> that by using 10 pulses of 20 microseconds length a 90% kill of *Saccharomyces cerevisiae*, *Candida utilis*, *Escherichia coli*, *Motile pseudomonad*, *Clostridium welchii* could be obtained with field strengths of 6-24 kV/cm. Short pulses were used to minimize water temperature rise (held to 10°C). It was considered by the authors that the electric field caused an irreversible loss of the membrane's function as the semipermeable barrier between the bacterial cell and its environment and thus caused the cell death, however, this could be a direct effect of electrophoresis interfering with the cell's metabolism on colloidal particles that might permeate the membrane or cell walls. Use of electrical fields in areas where biological treatment is being performed might have a detrimental effect on the biological organisms



and should therefore be approached with caution.

In summary, colloidal stability is the result of colloid charge which depends on the ionic adsorption of the colloid particle, and the Zeta-potential is the measure of this adsorption. Where natural agglomeration of colloidal particles based on the short range Van der Waals-London forces is desired, a low or zero Zeta-potential is sought to minimize particle dispersions. Counterwise, if synthetic coagulating agents, e.g. short and long chained polymers are to be used to tie or bind the particles by adsorption, then we are interested in the particle maintaining an opposite charge to the polymer surface charge character in order to obtain the necessary electrical bond for adsorption. It appears this concept is not well understood by many activities attempting to remove colloidal suspensions.



## CHAPTER V

### COLLOID REACTIONS IN MAGNETIC FIELDS

Colloids can be divided into three categories with respect to their reaction and relation to magnetic fields. One category are those colloids having no electrical charge or zeta potential and exhibiting diamagnetic properties - since this category has little or no reaction to a magnetic field it will not be considered further in this paper other than to note that the literature reviewed failed to give a guide or quantitative estimate of the number or percentage of such colloidal particles that could be expected to be found in natural and/or polluted waters. A second category, consisting of colloids having paramagnetic and ferromagnetic characteristics, has applications for employing magnetic fields and inducing magnetic attraction forces in the colloid suspensions in order to perform a physical act (e.g. increase flocculation, magnetic clutch action, particle alignment in the suspension). The third category consisting of particles having either paramagnetic or diamagnetic characteristics but carrying an electrical static charge or zeta potential charge while in the fluid medium will be investigated below to ascertain the extent of the reactions such particles will exhibit in a magnetic field.

The literature on colloids in magnetic fields and magnetized interaction of colloids in the U.S. and West Europe is considerably less extensive than that dealing with electrical fields. In the late forties Voet and Suriani<sup>31</sup> performed experiments using iron carbonyl globules



averaging 3 micron diameter in a nonaqueous vehicle (mineral oil and oleic acid to maximize dispersion characteristics). It was found that the dielectric characteristics gave a more accurate picture of particle orientation and agglomeration than did rheological data based on viscosity measurements since the shear necessarily applied in the latter case destroyed particle agglomeration. Application of a magnetic field to the sol resulted in linear chains of the iron particles being formed with an increase in the dielectric constant of the dispersion. With removal of the field magnetized particle chains remained but took up a more random orientation than when the field was applied. This suggests that a simple means of measuring whether a sample colloidal solution has favorable agglomeration characteristics in a magnetic field could be ascertained by measuring the dielectric constant of the solution with and without a magnetic field applied.

J. Pryce-Jones<sup>32</sup> ascertained, as forerunner to the magnetic clutch, that a dispersion of 25% by volume of black magnetic oxide of iron in oil has a considerable increase in viscosity when a magnetic field is applied. It was also determined that when an alternating current was applied to the coil producing the magnetic field, the viscosity was reduced.

Application of magnetic methods to water treatment have been confined almost exclusively to materials with high ferromagnetic properties and particles having diameters greater than 100 microns. Mining and steel processing plants utilize magnetic properties of their effluents to assist in removal of contaminants. As an example, the wash water used in a dust scrubber system can then be directed past permanent



magnets and the induced magnetism of the fine particles attract each other to induce agglomeration and flocculation. Where the colloidal particles have ferromagnetic characteristics, the use of a magnetic flocculation process greatly enhances the effectiveness and efficiency of removal of those particles as well as paramagnetic and diamagnetic particles that are entrapped during the agglomeration process. This means is also employed for recovery of valuable particles such as magnetite, ferrosilicons, nickel powder and mill scale. Where flocculating polymers are used to improve coagulation of nonmagnetic suspensions, seeding with fine ferromagnetic particles and then passing the flow through a suitable magnetic field will improve the formation of larger agglomerates and can result in savings through the use of less polymers and flocculating agents. Permanent magnetic flocculators have been developed by Eriez Magnetics, of Erie Pennsylvania who hold two patents on the process; #3,536,198 "Apparatus for Magnetic Flocculation of Agglomerates" (Oct. 27, 1970), and #3,549,527 "Method of Clarifying Aqueous Suspensions" (Dec. 22, 1970). Eriez Magnetics has found that optimized performance can be obtained under the following conditions:<sup>33</sup>

- "1. A satisfactory demagnetizing force (for most applications) of 450 rms oersteds at 60 cycles for 1/20 second duration will depolarize natural magnetite particles coarser than approximately 10 microns.
2. Effective flocculation of magnetite is obtained when a slurry with more than one percent magnetite is exposed for a period of approximately 1/15 second to a 600 gauss field.
3. Cost of demagnetizers (or flocculators) increases rapidly for larger diameter pipes. For reduced costs, narrow rectangular sections are recommended for magnetic flocculators.



4. Permanent magnetic flocculators are preferred to magnetizing coils since there is no operating cost and no maintenance required.
5. To select the correct magnetic flocculator (or demagnetizing coil) the following information is necessary:
  - a. Magnetic product susceptibility
  - b. Magnetic product coercive force
  - c. Percent of magnetic product in the solids (and percent of solids in the fluid)
  - d. Flow rate and viscosity
  - e. Structure of magnetic product

NOTE: Magnetic susceptibility is defined as the ratio of the intensity of magnetization produced in a substance to the magnetizing force of intensity of the field to which it is subjected.

Magnetic coercive force, normally given in oersteds, is the magnetic intensity required to magnetize a ferromagnetic material.

Oersted is the magnetic intensity that produces a force of 1 dyne on a unit magnetic pole, or the intensity 1 cm from a unit magnetic pole.

Remanence, normally given in gauss, is the magnetic induction remaining in a magnetized substance when the magnetizing force has become zero.

Gauss, is the flux density or magnetic induction equal to 1 maxwell/cm<sup>2</sup> (a maxwell is the flux through a cm<sup>2</sup> normal to a field at 1 cm from a unit magnetic pole). A field of 1 gauss will produce an emf of 1 abvolt in a 1 cm long conductor moving at a velocity of 1 cm/sec perpendicular to the field."

C & EN<sup>34</sup> reports that MIT is currently working on "high gradient magnetic separation (HGMS)" equipment which are designed to produce effect fields of 10 to 100 kilooersteds with gradients as large as 1 kilooersted per micron (as compared with drum separators with a field of 1 kilooersted magnetic field and field gradients of about 0.1 kilooersted per cm). The device is being tested in a batch-type process for removal of micron sized weakly magnetic titanium dioxide particles from kaolin clay. Other possible applications of the device envisioned are desul-



furization and deashing of coal, based primarily on removing weakly magnetic pyritic sulfur from a pulverized coal slurry. It is understood also that the Francis Bitter National Magnet Laboratory, MIT, is investigating the feasibility of using the equipment for water treatment by seeding with iron oxides with flocculants such as aluminum sulfate.

Dr. McLellon has in his personal library certain abstract translations of Russian, Czech, and German papers that relate to magnetic water treatment that are briefly summarized below:

- a. Parameters and information are given about the Czechoslovakian device for magnetic water treatment, MUV, which is equivalent to CEPI W of a Belgian firm, EPURO and which is suitable for treating of water with maximum of 200 mg/l of salts/liter. No inhibition of the surface corrosion caused by  $\text{CO}_2$  and reported for CEPI W was observed; only the corrosion by O was inhibited in some cases at an elevated temperature. This fact was caused probably by a protecting coat of  $\text{Fe}_3\text{O}_4$  formed from  $\text{Fe}(\text{OH})_3$  by the release of H. This reaction was more rapid in a magnetic field. CA65-18323h. Zdenek Matejka (1966 - Czech).
- b. Passing water through an electromagnetic apparatus with a magnetic field strength of 100-1000 oersteds increased the hydraulic grain size of the coagulated suspension. The magnetic field reduced hydration of ions formed from the dissolution of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{FeCl}_3$ . The degree of hydration was determined from the heat of dissolving. The maximum decrease was at 500-700 oersteds. The electrokinetic potential of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  sols changed upon application of a magnetic field; minimum potential was 500-700 oersteds. The change in potential was associated with a decrease in hydration. Associations of ions form and the electrical conductance of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{FeCl}_3$  solutions decrease in a magnetic field. Coagulation is more rapid in water in a magnetic field. CA64-13916f. A. I. Shakhov and S. S. Dushkin (1965 - Russian).
- c. A temporary modification of the water structure results in a measurable change in surface tension. This is brought about by a 10 kc electromagnetic field produced by a 10 watt generator and two containers filled with triply distilled water, one of them at 50 cm, the other at 10 m from the source. After a one-minute irradiation, the sample close to the source has a surface tension 1-2% below the normal value as given by the unaffected distant sample. This modification tends to disappear only very slowly. It is related to a change in the internal structure of water, but no



further analysis or explanation is given. CA54-12698h. Giorgio Piccardi - Univ. Florence (1959 - Italian).

- d. The facts showing that a magnetic field changes the structure and physical chemistry properties of solutions are presented, and the process of magnetic water-treatment is described. Hydration of salts is a very important factor in treatment of water, preventing high scum formation. CA58-1240c. V. I. Minenko and S. M. Petrov (1962).
- e. Earlier literature data on the effects of a magnetic field on the the physico-chemical properties of solutions contradict the First Law of Thermodynamics, by apparently finding physical effects much greater than are possible for the work done by the magnetic field. In experiments, no effects on the following were observed (strength of field in oersted given): temp. of H<sub>2</sub>O and 0.1M HCl (2000); soly (?) of CaSO<sub>4</sub> · 2H<sub>2</sub>O in H<sub>2</sub>O at 25° (3000); d. of H<sub>2</sub>O and M FeSO<sub>4</sub> at 25° (≤2300); or in the n of H<sub>2</sub>O (Piccardi, CA54-12698h - Minenko and Petrov, CA58-1240c). CA66-5812v. A. N. Kirgintsev and V. M. Sokolov (1966 - Russian).
- f. Decontamination of solutions containing radioisotopes is accomplished by adsorption on magnetic adsorbents and removal of the adsorbent from the solution by a magnet. Using adsorbents such as artificial magnetite or commercial products containing γ-Fe oxide, and carrier free radioisotopes, it was possible to remove 99% of the radioactivity from <sup>90</sup>Sr by using 4 - 50 mg samples of adsorbant with 1-day stirring of each batch; similar results were obtained with seven batches of adsorbent on <sup>60</sup>Co, while <sup>137</sup>Cs required 6 - 500 mg batches of adsorbent with 2-day stirring of each batch for similar removal. CA66-51301μ. Kurt Starke and Ch. Quecke (1966 - English).

On the basis of the above findings, the literature search was extended to more recent publications in U.S. and foreign periodicals. This search revealed that a very active and extensive research program in the use of magnetic fields for commercial applications is being carried out by the Russians with very limited development and research in the field being conducted by countries of the Western World. While a few suitable references were uncovered utilizing the Applied Science and Technology Index, the best index found for this subject was the Chemical Abstracts index which provided a brief summation of the articles, many of which (publications) were not available locally. Because of the



extensive coverage and limited time available, 1972 and 1973 indices were used and thus most of the papers were published in the period 1969 to 1972.

Of possible significance, of the eleven recent references to magnetic field structure and applications in the Western World, eight were summations of recent patent approvals. The thirty Russian and Iron Curtain country articles were "Journal-type" reports of institutional and commercial investigations - none were patents. A brief summary of the Western world patents and the other three papers follows:

- a. P. Goldberg, Jane, Hansford, & P. J. VanHurden, "Polarization of Light in Suspensions of Small Ferrite Particles in a Magnetic Field," J. Applied Physics, 42:3874-76 September 1971.

An unknown concentration of magnetite particles,  $\text{Fe}_3\text{O}_4$ , in a soap-like agent called "Ferrofluids" exhibited linear polarization (of light waves) characteristics when placed in a magnetic field of 2,000 gauss. Particles were sized at approximately  $0.02\mu$  and the light wave vector parallel to the magnetic lines of force was absorbed. It was found that the dichroic ratio,  $R_D = D_{\max}/D_{\min}$  where:

$$D_{\max} = \log_{10}(I_0/I_1) \quad \text{and} \quad D_{\min} = \log_{10}(I_0/I_2)$$

$I_0$  = intensity polarized light,  $I_1$  = transmitted light intensity  $D_{\max}$ ,  $I_2$  = transmitted light intensity for  $D_{\min}$  did not change with layer thickness of the ferrite particles or their number per  $\text{cm}^2$ . Water gave a wave-length dependant light scatter that, under favorable conditions, shows as a brilliant red. Line shaped agglomerations of the particles with line spacing of approximately  $0.4\mu$  are shown on micrographs.

- b. Almase, Gabriel Charles, Slusarczyk, William (Crucible, Inc.), "Apparatus and Method for the Removal of Magnetic Particles from a Liquid Stream," U.S. Patent 3,714,037 (C1 210/42; B 01d, 30 Jan 1973) - CA 128241g (1973).

Patent deals with a piping section that converts a cylindrical pipe to rectangular section having a "plurality of opposed electro-magnets" which provide the magnetic field.

- c. Carlson, Rolf C. (International Waterpure Corp.), "Removal of Colloids from Wastewater," Ger. Offen. 2,136,035, 1 Feb 1973 - CA 163787m (1973).



Colloids are removed from flowing wastewater by measuring the zeta potential in the liquid passing through a flocculation tank, injecting chemical additives for coagulation of the suspended impurities, passing the wastewater slurry through a settling tank and measuring the zeta potential in the line between the settling tank and an adjacent aeration plant. The amount of the required chemicals is controlled automatically by the zeta potentials measured at the two control points.

- d. Chervenak, Michael C. (Hydrocarbon Research, Inc.), "Solids Removal from Hydrogenated Coal Liquids," U.S. Patent 3,725,241 (Cl 208-10; C 10g, 3 Apr 1973) - CA 161949s (1973).

In the hydrogenation of coal under liquid-phase conditions by the expanded (ebullated) bed reaction process at 750° - 950°F and 500-500 psi H partial pressure, the removal of ash and unconverted coal is increased by passing the solids-liquid mixture (viscosity <50cP) through a 10,000 G magnetic field to attract the magnetically susceptible particles.

- e. Ustick, Daniel D., "Apparatus for the Separation of Ions from Solution," U.S. Patent 3,719,583 (Cl 204/301; B 01k, C 02b, 6 Mar 1973) - CA 151512e (1973).

An ionized solution to be treated, e.g. sea-water, is passed through a porous ceramic conduit. A magnetic field is maintained across the conduit by either a permanent or an electro-magnet. The ions, e.g. Na<sup>+</sup> and Cl<sup>-</sup>, pass through the walls to the outside where they are rinsed away by a parallel flowing current of unprocessed water. Desalination can be reduced to the extent required for subsequent use . . . The process meets minimum requirements for fresh water. (Author's comment: the description here is suspect or a very long conduit and very strong magnetic field is involved to provide the "ion" separation).

- f. Blaisdell, Donald Stapf; Klass, Ruth E. B., "Apparatus and Method for Treatment of Sewage," U.S. Patent 3,697,426 (Cl 210-42; B 01d, B 03c, 10 Oct 1972) - CA 19988k (1973).

Magnetic densification is achieved by adding cationic polyelectrolyte coagulants and magnetic weighing agents to sewage and densifying the coagulated solids under the influence of a magnetic field which may be either uniform or nonuniform, thus producing a clarified effluent. Example given: Village of 5,000 population in NE U.S. treated with 3 ppm reagent - a mixture of cationic starch, Mesabi hematite (80 mesh US std. screen) and anhydrous FeCl<sub>3</sub> in a weight ratio of 1:2:30 resp. Sewage and reagent thoroughly mixed, then split into two portions. One massed through "magnetic agglomerator" - a polyethylene funnel approximately four inches long with a 0.5 in. diameter outlet end, and a 3 in. diameter inlet and 100 turns of No. 16 insulated bell wire energized with 5 amp. of electric current. After passage



through "magnetic agglomerator" stood with second portion (nonmagnetized slurry) for 15 minutes. Obtained "almost double the volume of the settled solids in the second portion."

- g. Kaiser, Robert (Avco Corp.), "Ferrofluid Composition Usable to Control Oil Spills Floating on Open Bodies of Water," U.S. Patent 3,700,595 (24 Oct 1972) - CA 33689v (1973).

Finely divided magnetizable materials ranging up to about 300 Å in size, dispersed in saturated cyclic and aliphatic hydrocarbons having a boiling point above 100° and colloidally stabilized by a water-insoluble hydrocarbon oil-soluble surfactant. The ferrofluid has an interfacial tension, against water, not less than approximately 25 dynes/centimeter. To combat oil spills the compound is dispersed into the oil slick and a magnetic field is then used to remove, collect or mop up the oil.

- h. Siemens, A. G., "Removal of Iron Oxide from Water in a Steam Boiler Installation," Brit. 1,291,600 (Oct 1972) - CA 33768v (1973).

Feed water invariably contains magnetic oxides  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ . Removed using magnetic filter of at least 400 Oe. Uses annular coil, a.c., water flow 10-50 cm/sec. To clean, uses decaying a.c. of 50 to 60 Hz. Oxides are washed from demagnetized pieces by turbulent water flow aided by the introduction of air.

- i. Science News of the Week, Sci. News, 98:411, November 28, 1970.

A polymer material has been developed which permits examination of antiferromagnetic properties (a material having successive magnetic spin axis point in opposite direction. The material is tetramethylammonium manganese chloride (TMMC for short) with the formula,  $[(\text{CH}_3)_4\text{N}]\text{MnCl}_3$ , where the methyl ammonium acts as a magnetic insulator and the manganese chloride forms the magnetic chain. This article stated that neutrons possess magnetic fields and were used for investigating the magnetic structure of TMMC. Further it stated that in a magnetically ordered substance, the spins periodically change direction (like falling dominoes) and the phenomenon has the appearance of a wave, called the spin wave. It was hoped that further theory and experimentation would provide values for the magnetic force between ions.

- j. Dunlop, D. J., "Magnetite: Behavior near the Single-Domain Threshold," Science, Vol. 176:41-3 Reports section, 7 Apr 1972.

Maximum values for the single-domain threshold,  $d_0$ , and super paramagnetic threshold,  $d_s$ , in pure magnetite are found to be  $570 \pm 50$  and  $350 \pm 50$  angstroms, respectively. Particles larger than  $d_0$  but smaller than about 0.25 microns have size-dependent saturation remanences and coercive forces like those of multidomain particles, but



intense and stable thermoremanent magnetization like that of single domain particles. The presence of magnetite grains in this size range could account for the essentially single-domain character of stable natural remanence in many volcanic and intrusive rocks.

In grains  $0.1\mu$  ( $1000 \text{ \AA}$ ) the width of domain wall is a substantial fraction of the grain diameter. H. Amar (Phy. Rev. 111:149, 1958) calculated wall widths of 120, 160, 190, and  $225 \text{ \AA}$  in iron particles ( $d_0 \approx 150 \text{ \AA}$ ) having diameters of 200, 400, 600, and  $1000 \text{ \AA}$  respectively.

- k. Cadman, Theodore W. and Dellinger, Robert W., "Techniques for Removing Metals from Process Wastewater," Chemical Engineering, April 15, 1974, page 80.

U.S. Patent 3,511,776. "The invention, which is not limited to separating materials from seawater, uses electromagnetic radiation, preferably in the UV or X-ray spectra, to change the charge on ions in the water. Radiation of the proper wavelength strips electrons from the ions, reducing them to a higher ionization potential.

An electromagnet extending around the circumference of the pipe concentrates the ions in localized areas of the stream cross-section. Water at central regions of the flow is withdrawn through an outlet pipe, which deflects the water of lower ion concentration to outside the pipe. Water of higher ion concentration continues flowing through the pipe. A bar magnet with one pole located close to the side of the pipe cuts down on Brownian motion of the ions in water."

Foreign papers are grouped and summarized below with reference credit to authors and the Chemical Abstract ref. number given for source of information. The parenthetical date after the author's name provides the initial publication date of the article, if given.

- A. Physical and chemical changes of aqueous solutions in magnetic fields:
1. This Bulgarian article finds that at certain times magnetic treatment is without effect! CA77-38963. Milko Iovchev (1972 - French).
  2. In a nonuniform magnetic field of up to 1020 Oe the behavior of nickel, copper, and zinc ions was investigated, in a 16% aqueous sulfate solution. It was found that paramagnetic  $\text{Ni}^{++}$  and  $\text{Cu}^{++}$  ions were redistributed to regions of high magnetic field strength, while diamagnetic  $\text{Zn}^{++}$  was found in the weaker magnetic field areas. Migration scale of the ions exceeds molecular fluctuations associated with energy of thermal motion. CA77-67826g. Chernobai, V. L.; Orlov, N. A.; Vosil'ev, A. N. (1971 - Russian).



3. Under "definite optimal conditions" and during "definite time of a year" magnetic treatment will increase oxygen concentration. CA77-92688w. G. N. Khazhinskaya and others (1971 - Russian).
4. The dependence of impurity-particle concentrations on the magnetic field strength at temperatures of 10 - 85° (C assumed) fluctuates widely. CA72-156223a. L. M. Mikhel'son (1971 - Russian).

5. With the superposition of a magnetic field, the molecular motion of water, which is described by the equation,

$$\nu = (1.44 \times 10^3) p^2 \nu_H e^{-\epsilon/RT}$$

where  $\nu$  is the mean translational shifting frequency,  $\nu_H$  the water molecule vibration frequency in the equilibrium position,  $p$  the fraction of the H bond existence in water,  $\epsilon$  the activation energy of the cleavage of this bond, changed in such a way that  $\nu_H$  increased and  $\nu$  decreased. The density and viscosity of the water increased in the magnetic field, and the mobility and diffusion of the water molecule decreased. The diamagnetic properties of water were intensified in the magnetic field. The effect of the magnetic field on solutions was studied. The magnetic field made the ion distribution in a solution anisotropic (from the standpoint of short-range order). If the concentration of the solution is close to saturation point then over saturation of a solution will be observed with superposition of the magnetic field, i.e. magnetic treatment of a solution causes crystallization. The magnetic susceptibility of the solution in the magnetic field changed in the direction of increased diamagnetism. The structural forms and the equilibrium of the water were studied under natural conditions. CA75-8103s. B. M. Dolgonosov, Z. Ya. Yaroslavskii (1971 - Russian).

6. Magnetic treatment increased UV (ultraviolet) extinction of water. This was probably the result of an increase in cross linking of the water under magnetic treatment. CA78-8107w. G. M. Ivanova, Yn. M. Maklnev (1971 - Russian).
7. The crystal formation rate of H<sub>2</sub>O is affected by magnetic field strengths of 500 - 2500 Oe. The crystals are larger under the action of a magnetic field. Previous magnetic treatment of water results in the production of fine crystal ice and its structure can be controlled by an external magnetic field. CA78-8689n. L. A. Bantysh and others (1971 - Russian).
8. Impulse and pulsing magnetic fields increase the rate of crystallization-center formation only in the presence of ions, whereas no effect of the fields was found in deionized H<sub>2</sub>O. A constant magnetic field, however, caused a decrease in the rate both in the absence and presence of ions. In tap water and in deionized



H<sub>2</sub>O containing 0.028% KCl having the same electrical conductivity as the tap water, the rate doubled in value in a single impulse of 2500 Oe in approximately 0.4 sec at -12°. Pulsing field with changing from 1100 to 2000 Oe had same effect. The effect of a constant magnetic field of 2200 Oe was studied at -22 to 24°. CA78-8691g. V. G. Zaremba and others (1969 - Russian).

9. Magnetic treatment can be effective only if the field could be applied to water present in a supersaturated state based on CaCO<sub>3</sub>. In such water, going past a magnetic field, large ions appear and cause local changes in CO<sub>2</sub> solubility. As a result, negligible amounts of CaCO<sub>3</sub> separate around these large ions. CaCO<sub>3</sub> stabilizes the crystallization centers during the precipitation and deposits scale-forming agents in water. Rate of new center crystallization appearance for unit area at a constant temperature is directly proportional to the supersaturation of solution and to the square of field voltage. CA78-33743h. V. G. Dobczhanskii, Yu. A. Zaslavskii (1971 - Russian).
10. A quantized model for explanation of the effect of a transverse magnetic field on carrier distribution in samples of Mn- or Sb-doped Ge was presented. Analysis of theoretical results of the model showed that the oscillations of re-combination waves depend strongly on concentration and lifetime of carriers. The magnetic field deflects the carriers toward the surface, and surface re-combination is increased. The dependence of the change in condition in a magnetic field on the velocity of ambipolar drift of carriers,  $W_0$ , was determined for different magnetic and electrical fields. The change in carrier concentration was found from a plot of Hall constant versus  $W_0$ . Experimental results agreed very well with theory. CA78-103229w. I. V. Karpova and others (1972 - Russian).
11. Change in electric conductivity,  $k$ , of distilled water exposed to a constant magnetic field,  $B$ , for 30, 60, and 120 minutes at  $B = 450, 1500, 2000$ , and 2500 gauss was obtained at post-magnetization times,  $t_m = 0.5$  or 24 hours and at postdistillation times,  $t_d = 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$ , and 6.0 hours. A decrease of  $k$  by exposure for  $t = 120$  minutes and increase at  $t = 30$  minutes were established. The change in  $k$  was maximum at  $B = 450G$ ,  $t = 30$  minutes, and  $t_m = 24$  hours (+36.68). The electrical conductivity decreases with increasing  $t_d$ , depending on  $B$  and  $t$ . At  $t = 120$  minutes, the dependence of  $k$  on  $t_d$  is linear. CA78-89850h. S. I. Todocov and others (1969-70 - Bulgaria).
12. The magnetic susceptibility of water changes very little with a change of temperature within the limits of 5-25°. The completely different character of change of magnetic susceptibility of natural mineralized and distilled H<sub>2</sub>O with the voltage of the magnetic field indicates the simultaneous existence of two



mechanisms of action of the field (on the ions of the electrolyte and on the water itself). Magnetic treatment aids dissolving of air-oxygen in water until saturation, which leads to the change of some physical and physical-chemical properties of water. The greater the degree of mineralization of water, the greater the time of maximum secondary action and the time of relaxation of magnetic treatment. The basic cause of nonreproducibility of the effect of magnetic treatment is the extreme dependence of the effect on parameters of treatment: voltage of the field; rate of water (flow) and number of fields; and fluctuations of the salt content of the water. For effective application of magnetic treatment, constant control of the salt composition and corresponding of tuning or frequency trimming of magnetizing apparatus are necessary. CA78-101841r. V. E. Zelenkov, Yu. K. Chernov (1971 - Russian).

#### B. Boiler Feedwater Treatment:

1. No clear evidence for reduced scale formation using magnetically treated water was found (in comparison with untreated water). CA77-9497. L. S. Herbert (1969 - Austria).
2. Boiler make-up water was treated by magnetic field of 1500 Oe. A reduction in amounts of CaO and scale deposited were noted of <99.9% for tap water and <97% for chemically treated and deaerated Volga river water. Fraction of fine  $\text{CaCO}_3$  particles  $0.5\mu$  that remained dispersed in water, increased from 10 to 79.4% by increasing applied field from 500-1500 Oe. CA77-24703x. N. P. Lapotyshkina and others (1972 - Russian).
3. Similar reduction in scale deposit using laboratory water treated to a field of 1000 Oe, heat flux  $0.04 \text{ MW/m}^2$  in a  $1.6 \text{ g CaSO}_4/\text{kg}$  solution obtained approximately 85% scale reduction. Caspian Sea water gave 41% reduction at 1500 Oe and heat flux of  $0.1 \text{ MW/m}^2$ . CA77-24727h. O. I. Martynova, B. T. Gusev (1972 - Russian).
4. The effect of ferromagnetics on scale formation during magnetic treatment of water under industrial conditions gave "optimum" treatment condition of cooling water as: Magnetic field intensity =  $0.8 \times 10^5 \text{ A/m}$ , water velocity =  $0.4 - 1.0 \text{ m/sec}$ , ferromagnetic materials concentrations up to  $0.6 \text{ mg/l}$ . Operating cycle of condensers was 3 months without treatment, 5 months with  $0.1 \text{ mg/l}$ , and 12 months with  $0.6 \text{ mg/l}$  of ferromagnetic materials. The effect decreases during spring floods and autumn rains owing to the changes of salt compounds. CA78-47614. I. M. Fedotkin and others (1972 - Russian).



### C. Magnetic treatment of clay suspensions:

1. The effect of a magnetic field on the rate of sedimentation of activated carbon and clay was studied at field intensities of 80, 400, 640, and 960 A/cm (amperes/centimeter). The clay concentrations were 25, 100, and 250 mg/l,  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{FeCl}_3$  as a flocculant were 25, 50, 75, and 100 mg/l, and pH was 6.4-6.7. The flocculation rate increased 1.5 - 2 times, the degree of purification of water 1.5 - 2.5 times with a decrease of flocculant consumption by a factor of 2-3. The optimum magnetic field intensity is 400 A/cm. CA78-75717h. E. D. Babenkov, E. I. Kersanova, V. E. Gurtovenko (1972 - Russian).
2. Precipitation intensification of fine, clay slurry from saturated potassium and sodium chloride solutions. Applying a magnetic field (from a coil) current intensity <3a. at <2100 Oe, pulp flow through magnetic field = 0.65 m/sec(!). At 1200 Oe precipitation rate increased 9-14% (this was peak field strength). Optimum liquid/solid ratio 15. Also additional optimum obtained by adding approximately 2.5 g/m<sup>3</sup> of polyacrylamide flocculant. CA78-99819u. Yu. Z. Zinov'ev, B. D. Nekrasov (1972 - Russian).
3. The sedimentation of the fine dispersed clay particles of a suspension was examined using a magnetic apparatus of the solenoid type at 0-600 Oe at a rate of 0.5 m/sec through the apparatus. The content of magnetic particles in the clay was 4-11.8%. In the beginning of the test the upper border sinks slowly because the formation of the initial structure of the clay suspension after the intensive stirring. In the next stage the border sinks more quickly (12-20%)(?). CA78-139618m. I. E. Zamyatina, I. I. Orlov (1970 - Russian).

### D. Concrete and building material applications:

1. Approximately 5% less cement and 3-13% improved strength was obtained using a two stage magnetically treated water. CA77-117585u. B. Shevchuk, S. Kligman (1972 - Ukrain).
2. Concretes were made with water passed through magnetic field at a rate of 0.5-1.0 m/sec. Magnetic treatment reduced amount of water required and increase plastic strength (a function of magnetic field, velocity of flow, salt content in water). Depending on composition of the mixture, increased strength after 1 day was 56-98 and after 28 days 101-6 kg/cm<sup>2</sup>. CA77-24242w. Ya. L. Aradovskii and others (1972 - Russian).
3. At 2200-2400 Oe and temperatures of 70-110° the solubility of all  $\text{CaSO}_4$  (Gypsum) modifications ( $\text{CaSO}_4$ ,  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  &  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in magnetized water was much lower than in common water and the separated crystal,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  had a more



fine-crystal structure. CA78-33396. P. S. Chechel, G. V. Annenkova (1972 - Russian).

4. The effect of a magnetic field on properties of distilled water, tap water and solutions of  $\text{Ca}(\text{OH})_2$  for manufacture of building materials with and without additions of  $\text{Fe}^{++}$ . Changes in dielectric constant of tap water treated with constant magnetic field are shown. A comparatively weak magnetic field has the greatest effect on the change in the dielectric constant. The amount of lime absorbed by silicic acid from a  $\text{Ca}(\text{OH})_2$  solution treated in a magnetic field exceeds somewhat that absorbed from an untreated  $\text{Ca}(\text{OH})_2$  solution. Water treated in a magnetic field changes the stability of the gas-silicate samples from -16 to +23%. CA78-88175e. H. Elzbutas and others (1971 - Russian).
5. Ash and slag from combustion of . . . brown coals were tested as structural materials. The high  $\text{CaO}$  content of the ash and slag (19-36%) makes it possible to use them as binders. Hydration of the material was accelerated by use of magnetically treated water with and without 3%  $\text{HCl}$ . Cubes made from these materials hardened in 28 days. Magnetic treatment of the water and addition of  $\text{HCl}$  increased the compression strength from 33-75  $\text{kg/cm}^2$  to 282-309  $\text{kg/cm}^2$ . CA78-87015r. A. T. Logvinenko, M. A. Savenkina (1971 - Russian).

#### E. Coal filter application:

1. Use of magnetic treatment of a coal floatation concentration solution while employing auxiliary reagents (raffinate oxidate and a gas condensate) during filtration permitted an increase in the filtration rate and increased the productivity of the filters in industrial application by approximately 33%. CA78-113692f. V. S. Kaminskii and others (1971 - Russian).

#### F. Water and wastewater beneficiation applications:

1. Oils and resins are removed from wastewaters by adsorption onto magnetically susceptible powders, e.g. magnetite, and removal of the powder with a magnetic separator. CA78-33695. E. V. Prevalov and others - U.S. Patent 350,758 (Sept 1972).
2. Results of magnetic treatment of pulps in the Kaxmekhanobr Institute during beneficiation. Magnetic treatment either accelerated the precipitation of solid phase or has stabilizing effect on the system depending on ion composition and the presence of colloids and mechanical suspensions. The stable technology effect was observed in the presence of complex-forming ions ( $\text{Zn}$ ,  $\text{Fe}$ ,  $\text{Al}$ , etc.) during magnetic treatment of stable aqueous systems. CA78-87389r. Yu. A. Mast'yanov (1971 - Russian).



G. Metal and miscellaneous applications:

1. Magnetic treatment of industrial wastes from chloro-organics production obtained significantly increased precipitation of suspended matter from waste containing Fe,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Cl}^-$  at pH 8.9 when passed through strong magnetic field. CA77-24581f. A. I. Shakhov, S. S. Dushkin (1972 - Russian).
2. Copper extraction from ores was increased by 1.32% after magnetic treatment (1400-1600 and 200-2400 Oe) of 8% Xanthate solutions. CA78-87386n. V. M. Arashkevich and others (1971 - Russian).
3. Scrubber waste waters from the wet purification of gases from open-hearth furnaces were treated by a magnetic field of  $8.5\text{--}12.0 \times 10^4$  A/mm. The wastewaters contained suspended particle concentrations of 1000-2000 mg/l, with an average magnetic permeability of 3.9, a residual induction of 195G and an intensity of 125 Oe. The direction of the flow (flow rate 2.0 m/sec) was altered to allow four crossings of the magnetic zone. The clarification effect on the treated water was >95% at a sedimentation rate of 0.2 mm/sec. CA78-163673w. A. I. Shakhov and others (1973 - Russian).

Use of translation abstracts leaves much to be desired in that one is at the mercy of the translator's interpretation and statements he considers to be pertinent. In spite of the short comings of such data, one gets an impression of almost an obsession on the part of the Russians to utilize a magnetic field for treating water and a general lack of positive identification of the magnetic field's contribution versus electrolytes and coagulating agent contributions. It would appear, however, that there is adequate justification for greater effort being exerted in countries of the West on magnetic field applications that would enhance and improve our pollution control methods and processes. The Russian translations and data should be a guide to some of the pitfalls to be expected and to areas offering good "pay-offs."



## CHAPTER VI

### ANALYSIS AND CONCLUSIONS

As a result of this review of the current state of knowledge of colloids and the reaction and employment of electromagnetic fields in water treatment, one is faced with the questions: "When should electromagnetic processes be employed in water and wastewater treatment?" and "Which are the areas that require further study and research and offer promise of providing needed, improved, and economic treatment capabilities?"

The character and nature of unwanted colloids and suspensions is the initial determining factor as to what process is best suited for their removal. Where these particles have ferromagnetic characteristics the use of a magnetic field to magnetize the particles will enhance their flocculating tendency and thereby assist in recovery and/or removal. Most compounds of Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Titanium (Ti), Uranium (U), Vanadium (V), and the rare earths Cerium (Ce - atomic number 58) through Ytterbium (Yb - atomic number 70) exhibit positive magnetic susceptibility. However, some of these compounds exhibit antiferromagnetic properties depending on temperature and the oxidation number (valance) involved in the compound. Examples of compounds having antiferromagnetic properties are:  $\text{CoCl}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{FeO}$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{MnO}$ ,  $\text{NiCl}$ ,  $\text{NiO}$ ,  $\text{TiCl}_3$ , and  $\text{V}_2\text{O}_3$ ; however, except for  $\text{Cr}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\text{NiO}$ , the Neel



temperatures are less than  $0^{\circ}\text{C}$  and therefore the compounds would exhibit paramagnetic properties in water solutions.

In those instances where ferric compounds are utilized as coagulating and flocculating agents, consideration should be given to magnetizing the sol as available evidence indicates that improved coagulation with reduced agent usage can be achieved in most cases. The economic trade-off of magnetizing equipment installation cost versus operating cost savings would of course have to be investigated. When chemical coagulation processes are being considered or investigated, especially when ferric compounds are involved, the use of a magnetizing process should be tested along with variations in pH, dosage and different agents. Application of a magnetic field either by use of a permanent magnet or a solenoid type to glass jars on a paddle stirrer appears to be a simple and inexpensive way of ascertaining if magnetic treatment has a potential benefit for a planned beneficiation objective. Consideration should also be given to the manufacture of polyelectrolytes containing ferromagnetic elements in the molecular chains that would further improve the efficiency when used as a flocculating agent. Russian experience would indicate a relatively weak field of less than 1,000 Oe is usually sufficient with maximum field strengths of about 2,400 Oe. It would also appear that equipment utilizing permanent magnets, such as manufactured by the Eriez Magnetics would provide minimum maintenance and operating costs.

The Russian interest in the effect of magnetic fields on calcium compounds triggered an investigation of the susceptibility of calcium



and its compounds where it was discovered that pure calcium as a solid is paramagnetic while all compounds of calcium were diamagnetic. Which leads to the question, "Could the magnetic effect on calcium occur only on the calcium ion?". A look at potassium revealed similar characteristics in that in its elemental state it is slightly paramagnetic but in compound form it is diamagnetic (except for ferricyanide,  $K_3Fe(CN)_6$ ; a chromate,  $K_2Cr_2O_7$ ; and the oxides,  $KO_2$  and  $KO_3$ ). In fact a comparison of the elements in the periodic table with the susceptibility data revealed that, except for hydrogen, all the elements in groups IA, IIA, IIIB through VIIB, and VIII are paramagnetic in their elemental state. All of these elements exhibit positive valence or oxidation states (except Rhenium which can exhibit a -1 valence) and would therefore form cations in solution. Elements in groups IB, IIB, IIIA (except Aluminum and Gallium in its liquid state at  $313^{\circ}K$ ), IVA (except white tin), VA, VIA (except oxygen and sulfur in its gaseous state above  $828^{\circ}K$ ), VIIA (except atomic iodine at temperatures above  $1303^{\circ}K$ ), and VIIIA exhibit diamagnetic properties in their elemental states and can have both positive and negative oxidation states of valences. It should also be noted that copper, while diamagnetic in the elemental state, is moderately paramagnetic in most compounds of copper. It would therefore appear possible that cations of paramagnetic elements might exhibit their magnetic properties in a magnetic field, however no literature was found to support this hypothesis.

On the basis that most, if not all, organic compounds are diamagnetic, magnetic treatment for beneficiation purposes will have little value without the addition of a suitable magnetically susceptible agent



or polyelectrolyte. In all cases of magnetic treatment it would appear desirable to minimize the zeta potential having available a large proportion of counter ions to reduce the repulsive forces between the colloid particles.

Electrophoresis does not appear to hold much promise at this time for water beneficiation use. The process capability to discriminate between different colloidal particles is based on the small electrical forces acting on relatively large masses in the colloidal particle over long time periods and thereby achieving a separation of like particles. Since the solution must remain electrically balanced and the counter ions remain in the vicinity of the charged particles, separation on a macro scale does not appear practical at the current state of knowledge unless some form of electrolysis is also involved in the process. However, activities performing jar tests and using coagulating agents and synthetic polyelectrolytes and polymers should have a thorough understanding of Zeta-potential and the colloidal agglomeration process they wish to achieve. Much of the literature fails to completely characterize the colloids and sols under study which account for much of the confusion and inability to duplicate results. Characterization of the waters under study for chemical treatment should include: pH, conductivity, zeta-potential, acidity/alkalinity as well as chemical composition, dosages, concentrations, and settling characteristics of the floc.

Potential areas of application of magnetic fields have been discussed and reviewed; however, research and valid data are very limited at present thereby limiting predictable results from such applications.



## CHAPTER VII

### POTENTIAL RESEARCH AND EXPERIMENTS

As commonly results from investigations similar to this, "the more knowledge one acquires, the less one knows," i.e. one recognizes many additional areas of investigation that could be examined and thereby improve our understanding of natural phenomena. In addition, certain experiments designed to demonstrate certain phenomena also come to mind and are presented in this chapter for the interested student who may wish to follow one of the "bypaths" that the author was unable to pursue.

#### A. Magnetic Characteristic Computer Model

It appears to the author that the chemical-physical sciences are reaching an overlapping stage wherein the "art" of chemical synthesis will soon be displaced by mathematical physics. Magnetic phenomena have normally been considered a part of the physical sciences, yet as was shown in Chapter II, it is related closely to chemical composition and state. Literature research in the area of atomic and molecular structures, the orientation and number of unpaired electron and their orbits in relation to temperature and magnetic characteristics, the orbital magnetic contributions to paramagnetic and diamagnetic materials would probably uncover more than the limited investigation of the author as to the state of our current knowledge. It appears to the author that this system would lend itself to computer simulation or modeling with



relatively little effort in view of the current close correlation of magnetic moments between those calculated based on electron spin only and experimental evidence.

Large quantities of magnetic susceptibility data exist in the CRC Manual for numerous elements and compounds. Further, the chemist's knowledge of atomic and molecular structures has been greatly enhanced in recent years with electron and nuclear magnetic spectroscopy availability. It thus appears to the author that the knowledge and evidence exists today that is required to formulate an equation or simulation model that could be used to predict magnetic characteristic for given atomic and molecular structures. Contrawise, the model could be utilized for determining the structures of complex molecules from their chemical composition and magnetic characteristics.

#### B. Magnetic Lens

The question arose in the author's mind (as it probably has in many others) whether magnetism - and gravity - were propagated at some fixed velocity similar to light; and that diamagnetic and paramagnetic properties might be likened to transmissibility of light through various mediums. If it could be shown that magnetic flux had a refractive index when moving from one material (air) to another (say iron) one could then construct a lens which would concentrate the flux to high concentrations or densities that could have many interesting applications and could possibly lead to other experiments designed to determine the velocity of such fields.



### C. Electrically and Magnetically Inert Colloids

As noted on page 47, the literature researched dealt exclusively with colloids that responded to electrical or magnetic fields, and from a "positive" sense viewpoint this was to be expected, since the subject matter was only interested in such reactions. However, nowhere in the literature reviewed was reference made to the proportion, numbers composition, or percentage of colloidal particles in a solution that would not respond to such fields. A study of colloidal particles to determine the number or percentage and composition of particles not subject to reactions in an electrical or magnetic field would appear to be of value, if only to indicate the value and emphasis that should be placed on investigations of electrical and magnetic colloid phenomena.

### D. Potential Laboratory Experiments

It appears possible to conduct some simple experiments in the laboratory here at FTU to obtain some experience and expertise as well as some quantitative data and confirmation of some of the Russian data. Some simple experiments are outlined below:

1. Jar tests of influent and effluent from the FTU secondary treatment plant varying the pH, coagulating agent concentrations, with and without an applied magnetic field, steady, pulsed, and alternating. While of necessity an analysis of the sol both before and after treatment would be required to determine any quantitative effects, it is expected that the variations in samples tested would tend to confuse the data and only qualitative results might be expected, albeit this could provide incentive and justification for additional and more thorough



tests. The laboratory shop has available two very strong permanent magnets (actual strength is not inscribed on the magnets) that appear to provide sufficient field strengths for jar tests. Pulsed and alternating fields could most simply be obtained by wrapping the jar with suitable turns of bell wire and using properly instrumented (to obtain volts, amperes, and time) rectifier and transformers to obtain the pulsed and alternating fields. The dielectric constant of the sol should be measured.

2. An extension of the above experiment or possibly an initial experiment would be to perform the tests described in 1 above using synthetically prepared colloidal solutions from distilled and deionized water where the various parameters of colloidal materials,  $\zeta$ -potential, pH, ionization, magnetic materials could be measured and controlled. These tests could investigate some of the Russian findings of precipitation of supersaturated salts and the effect of magnetic fields on calcium ions and solutions.

3. Third stage laboratory tests would involve use of the FTU Treatment Plant model, with and without ferrous coagulating agents and with and without magnetic field applications. Potential locations for the magnetic field application would be (a) in the line between the contact tank and the clarifier, (b) in the clarifier effluent at the chlorinator channel (since the effluent from the chlorinator is collected in bottles from the model, sedimentation in the bottles would have to be compared), and (c) location in the line to the digester or in the digestion tank might enhance dewatering characteristics of the sludge.



It is understood that the Natural Sciences Department has a very powerful electromagnet (with a small air gap) that could be made available, however the complexity involved in using this magnetic source does not appear justified at this time in view of literature evidence that very strong fields are unnecessary and do not provide optimum results.



## APPENDIX I

## HYPOTHETICAL ELECTROPHORESIS CALCULATIONS

Most of the literature reports results of experiments in the form of graphs and statements, calculations and dimensional disciplines are usually left for a reader's exercise. A better and more thorough understanding of the electrophoresis phenomena can be achieved along with an appreciation for sizes and quantities of the parameters involved can be obtained by performing such calculations on a hypothetical situation. Assumed values are underlined in the following problem.

Values and dimensions of equipment parameters for a water flow of  $Q = \underline{50,000 \text{ gpd}}$  are to be determined based on the assumption that it is desired to move all negatively charged colloidal particles 1 cm. to the side of a 2 cm. channel and thus concentrate the negatively charged particles to one side of the channel and the positively charged particles on the other side - similar to a reverse osmosis process, a divided flow channel could then physically separate the concentrations. The conductivity, the dielectric constant, zeta potential of particle, size/shape of particle, charge density of particle, pH, temperature, and ionic concentration of the surrounding medium are all parameters in determining the electrophoric mobility of a particle.

$$50,000 \text{ gpd} (4.38 \times 10^{-8}) = 21.9 \times 10^{-4} \text{ cu.m/sec} \times 10^6 = 2190 \text{ cc/sec}$$

Using the electrophoric mobility of a protein which has a velocity of  $20 \times 10^{-5} \text{ cm/sec}$  in a field of 1 volt/cm as a representative



colloidal particle,<sup>35</sup> an applied d.c. voltage of 500 will be reduced by the fluid dielectric constant, 1.87 for water to give a field strength in the 2 cm. channel of  $500/(2 \text{ cm})1.87 = 133.8 \text{ v/cm}$ . Particles in the hypothetical channel will therefore have velocities of the order  $133.8 (20 \times 10^{-5}) = 2.67 \times 10^{-2} \text{ cm/sec}$ . To minimize short-circuiting in the channel and turbulent flow a low channel velocity is desirable; also this leads to increased exposure time to the "plate" created electrical field. However, the higher the velocity the greater the plate sides will have to extend. Assuming a channel height of 2 meters = 200 cm, the cross-sectional area will be  $400 \text{ cm}^2$ . For a field exposure time = 2 minutes = 120 seconds, we obtain a velocity:

$$v = (2190 \text{ cc/sec})/400 \text{ cm} = 5.475 \text{ cm/sec}$$

and a length of channel =  $5.475 \times 120 = 6.57 \text{ meters}$  (or approximately 20 feet). If we assume the water to have a specific conductance,  $L_a = .00231 \text{ mhos}$  (this is equivalent to a NaCl gm-equivalent concentration = 0.02)\*. A resistance,  $\Omega = 430 \text{ ohms/cm}$  or 860 ohms for the 2 cm gap will exist, which results in a current flow =  $500/860 = .58 \text{ amps}$  or about 290 watts of energy.

Obviously, the one dimension that appears out of proportion for a facility of this nature is the maintenance of a 2 cm gap between two electrode plates having dimensions of approximately 6 ft. x 20 ft. with channel flow between them and a dividing segment at the down stream end

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\* Thomas M. Riddick, technical director for the Zeta-Meter Corporation in the Zeta-Meter Manual gives the following specific conductivity values for the various natural systems: fresh water rivers and lakes - 50-1,000  $\mu\text{mhos}$ ; human blood and lymph -  $\sim 12,000 \pm ? \mu\text{mhos}$ ; aqueous fluids of plants & trees - 3,000-8,000  $\mu\text{mhos}$ ; human urine, daily variation - 12,000-36,000  $\mu\text{mhos}$ ; ocean water - 60,000  $\mu\text{mhos}$ .



of the plates to separate colloid concentrations adjacent to either plate. By increasing the distance between the electrode plates the field intensity is decreased, thereby decreasing the colloidal cross-channel velocity and at the same time increasing the distance for separation. With the accompanying decrease in stream velocity resulting from the increased cross sectional area, and providing the plate length is adjusted accordingly, the following parameters could be expected for a 4 cm gap between plates:

Effective field voltage - 66.9 v/cm (500 v applied)

Cross stream velocity component -  $1.33 \times 10^{-2}$  cm/sec

Time to cover 2 cm approximates 80 seconds

Stream flow velocity -  $2190/800 = 2.74$  cm/sec

Plate length is again 2.19 m, but current flow is reduced to 0.29 amps and 145 watts.



## APPENDIX II

### SYSTEMS, QUANTITIES, AND UNITS

Engineers and scientists who do not work consistently in the electrical and magnetic disciplines are frequently confused by units and quantities of terms used in these fields. A very thorough and excellent description of the different systems used is contained in the CRC Handbook of Chemistry and Physics.<sup>36</sup> Excerpts from this description along with some of the more common conversions are presented below for use in practical applications of formulae and theory.

"The CGS system with three basic units (cm, g, s) and the MKSA unit system with four basic units (m, kg, s, A [ampere]) correspond respectively to two different sets of equations in the field of electricity and magnetism, which are developed starting from three and from four basic quantities respectively . . ."

"1. Systems of equations with three basic quantities. Three distinct sets of equations with three basic quantities have been developed in the field of electricity and magnetism. These are:

(1.a) The 'electrostatic system' of equations, defining the electric charge on the basis of Coulomb laws for the force between two electric charges, by taking the permittivity in vacuo equal to a dimensionless quantity, the number unity.

(1.b) The 'electromagnetic system' of equations, defining the electric current on the basis of the interaction law for the force between two electric current elements, by taking the permeability in vacuo equal to a dimensionless quantity, the number unity.

(1.c) The 'symmetrical system' or Gaussian system of equations, using the electric quantities from system (1.a) and the magnetic quantities from system (1.b). As a result of combining the two sets of quantities the velocity of light in vacuo appears explicitly in some of the equations interrelating electric and magnetic quantities."

"2. Systems of equations with four basic quantities. In the



equation with four basic quantities at least one quantity of electric or magnetic nature is included in the basic set. In such a system the permittivity and the permeability in vacuo appear explicitly as physical quantities with dimension in the relevant equations . . . "



COMMON (INTERNATIONAL) SYMBOLS, UNITS,  
AND NOMENCLATURE

<u>Symbol</u>	<u>Name</u>	<u>Abbreviation</u>
l,b,h	centimetre (CGS) metre (MKSA)	cm m
t	second	s
m	gramme (CGS) kilogramme (MKSA)	g kg
f,v	hertz ( $= s^{-1}$ )	Hz
F	dyne ( $= g \cdot cm/s^2$ ) (CGS) newton ( $= kg \cdot m/s^2$ ) (MKSA)	dyn N
E,U,W,A	erg ( $= g \cdot cm^2/s^2$ ) (CGS)	erg
E	joule ( $= kg \cdot m^2/s^2$ ) (MKSA)	J
(CGS SYSTEM)		
H	oersted ( $= cm^{-1/2} \cdot g^{1/2} \cdot s^{-1}$ )	Oe
B	gauss ( $= cm^{-1/2} \cdot g^{1/2} \cdot s^{-1}$ )	G
$\Phi$	maxwell ( $= cm^{3/2} \cdot g^{1/2} \cdot s^{-1}$ )	Mx
(MKSA SYSTEM)		
I	ampere	A
Q	coulomb ( $= A \cdot s$ )	C
P	watt ( $= J/s$ )	W
V	volt ( $= W/A$ )	V
C	farad ( $= C/V$ )	F
R	ohm ( $= V/A$ )	$\Omega$
L	henry ( $= V \cdot s/A$ )	H
$\Phi$	weber ( $= V \cdot s$ )	Wb
B	tesla ( $= Wb/m^2$ )	T



## CONVERSION FACTORS

<u>To Convert From</u>	<u>To</u>	<u>Multiply By</u>
Oersteds	Ampere-turns/inch	2.0212678
Oersteds	Ampere-turns/meter	79.577472
Oersteds	E.M. cgs. units magnetic field intensity	1
Oersteds	E.S. cgs. units	$2.997930 \times 10^{10}$
Oersteds	Gilberts/cm	1
Oersteds	Oersteds (Int.)	1.000165
Gausses	E.M. cgs. units magnetic flux density	1
Gausses	E.S. cgs. units	$3.335635 \times 10^{-11}$
Gausses	Gausses (Int.)	0.999670
Gausses	Maxwells/sq. cm	1
Gausses	Line/sq. cm	1
Gausses	Line/sq. inch	6.4516
Gausses/oersteds	E.M. cgs. units of permeability	1
Gausses/oersteds	E.S. cgs. units	$1.112646 \times 10^{-21}$
Gilberts	Ampere-turns	0.79577472
Gilberts	E.M. cgs. units of magnetic potential	1.
Gilberts	E.S. cgs. units	$2.99793 \times 10^{10}$
Gilberts	Gilberts (Int.)	1.000165
Gilberts/cm	Ampere-turns/inch	2.0212678
Gilberts/maxwell	Ampere-turns/weber	$7.957747 \times 10^7$
Gilberts/maxwell	E.M. cgs. units of reluctance	1.
Gilberts/maxwell	E.S. cgs. units	$8.987584 \times 10^{20}$
Maxwells	E.M. cgs. units of induction flux, lines, or Gauss-sq. cm	1.
Maxwells	C.S. cgs. units	$3.335635 \times 10^{-11}$
Maxwells	Maxwell (Int.)	0.999670
Maxwells	Volt-seconds, or Webers	$1. \times 10^{-8}$
Weber	Mks. units of induction flux, volt-seconds	1.
Weber	E.M. cgs. units of induction flux, lines, or maxwells	$1. \times 10^8$



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- <sup>7</sup>Milan Bier, ed., Electrophoresis (New York: Academic Press, Inc., 1959), p. 429; also an excellent discussion is given in Mysels, Introduction to Colloid Chemistry, pp. 359-363.
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- <sup>20</sup> Ibid., p. 423.
- <sup>21</sup> Ibid., pp. 428-432.
- <sup>22</sup> Weast, CRC Handbook, E69-72.
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